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OF

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133
28 AUG 1934
CALCUTTA... LATORS

1921. Vol. CXIX. — Pt-I

LONDON:
GURNEY & JACKSON, 33, PATERNOSTER ROW, E.C. 4.
1921.

PRINTED IN GREAT BRITAIN BY
RICHARD CLAY & SONS, LIMITED,
BUNGAY, SUFFOLK.

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AUG 2003
AUG 20
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1921. Vol. CXIX. Part I., pp. 1–949.

LONDON:
GURNEY & JACKSON, 33, PATERNOSTER ROW, E.C. 4.
1921.

4 FEB 2006

Printed in Great Britain by
Richard Clay & Sons, Limited,
Bungay, Suffolk

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JOURNAL

OF

THE CHEMICAL SOCIETY.

TRANSACTIONS.

Some Properties of Explosives.

A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON DECEMBER 16TH, 1920.

By SIR ROBERT ROBERTSON, K.B.E., F.R.S.

COMPARED with other branches of chemistry, the subject of explosives has received less attention than many. This is due to the risks attaching to their investigation, which requires costly safety precautions, and to the somewhat restricted and specialised field of application.

The late war provided a great stimulus to the investigation of explosives. Methods of manufacture of certain substances were brought to a very high degree of perfection, and processes of filling and application were carefully worked out, but much of this work was of necessity directed to the practical side.

A large field of research on fundamental principles, essential to future progress, remains for investigation.

It is proposed in this lecture to describe some steps that have been taken, both before and during the war, to obtain an insight into the principles of explosive phenomena by quantitative measurements of some of the more important properties of explosives, the work for the most part having been carried out at the Research Department, Woolwich.

Before discussing these measurements, it may be well to define what is understood by the term explosive, and this is conveniently done by stating that its function is to exert a sudden intense

pressure on its surroundings when suitably activated. This pressure is developed by the decomposition of the explosive into gas, with concomitant liberation of heat. It follows, therefore, that the fundamental features possessed by an explosive are:

(i) *Potential energy in virtue of its chemical constitution,* independent of external agencies.

(ii) Formation of gaseous products with simultaneous liberation of energy.

(iii) Rapid decomposition when suitably excited.

The investigation of the first of these involves a study of the thermochemistry of different types of chemical compounds, determination of heats of formation, and heats of explosion. On these properties depend directly the power and sensitiveness of the explosive, and indirectly the chemical stability. Thus the exothermic character of the decomposition of an explosive renders it liable to break down at the ordinary temperature, so that if the whole of the heat were conserved, the temperature of the explosive and rate of decomposition would be gradually raised to a pitch when explosion would spontaneously occur.

The investigation of the second involves the study of the chemical reactions attending all rates of decomposition up to explosion, and the equilibria established among the decomposition products, at different temperatures and pressures.

The investigation of the third involves measurement of the rate of propagation of the explosion wave and all the phenomena in the proximity of the detonating mass of explosive. This rate of propagation in the explosive largely determines the pressure developed, and is the criterion for classification of explosives as either high or low explosives. It has therefore a close connexion with the effects that they produce.

It is the object of this lecture to consider, in the first place, some of the properties of explosives, with special reference to the chemical constitution and the physical properties of the compounds themselves. An attempt will be made to trace a reflection of the molecular arrangement of the compounds in such important properties as the heat of formation, the chemical stability, the sensitiveness, and the violence that explosives exhibit.

A second part will deal with the constants and properties of the amatols, in view of the importance that they assumed during the war.

PART I.

The Influence of Constitution and Physical Condition.

The principal properties that will be considered, in conjunction with structure, composition, and physical form, are those of:

(1) Heat of formation.
(2) Heat of explosion and gases evolved.
(3) Chemical stability.
(4) Sensitiveness to shock.
(5) Rate of detonation.
(6) Pressure developed.

Special methods for determining most of these properties have been evolved in the Research Department, Woolwich, and it is these that have furnished most of the recently obtained data quoted in the sequel.

In each case a short account of the methods employed will be given before proceeding to the discussion of the properties.

(1) *Heat of Formation.*—The necessity for meeting certain requirements in explosive compounds, such as rapidity of action, stability on storage, and convenience of handling, imposes conditions which lead to a sacrifice of the original energy of combustion of the elements of which the explosive is composed.

In considering the thermal data, it is instructive to compare an explosive with a system containing carbon and hydrogen in the same ratio as they exist in the explosive, together with sufficient oxygen for their complete combustion. Such a system is found

TABLE I.

Heat of Explosion or Combustion of 1 Kilo.

One kilo. of the following system.	Heat in kg. cal. (water gaseous). Explosion.	Combustion.
(1) Glyceryl trinitrate	1478	—
(2) Carbon and hydrogen, in ratio as in glyceryl trinitrate, together with oxygen for complete combustion	—	2420
(3) Elements present in glyceryl trinitrate	—	1885
(4) Trinitrotoluene	924	—
(5) Carbon and hydrogen, in ratio as in trinitrotoluene, together with oxygen for complete combustion	—	2278
(6) Trinitrotoluene, together with oxygen for complete combustion	—	2009
(7) Elements present in trinitrotoluene, together with oxygen for complete combustion	—	2035
(8) Trinitrotoluene, together with ammonium nitrate for complete combustion	1004	—

to evolve considerably more heat for the same weight than the explosive itself, and this is due to the handicap imposed by the heat lost by forming the explosive from its elements, to want of oxygen for total combustion, to dilution with nitrogen, or to a combination of these.

It will be seen from the table [(1) and (2)] that the system of carbon, hydrogen, and oxygen corresponding with glyceryl trinitrate evolves for the same weight 64 per cent. more heat than this powerfnl explosive can evolve.

Conceiving the steps in its formation from carbon and hydrogen to propane, thence to glycerol, and thence to glyceryl trinitrate, energy is successively locked up in forming them, but chiefly during the process of hydroxylation of propane. The loss due to the heat of formation of glyceryl trinitrate as given by the difference between its heat of explosion (1) and that of the combustion of its elements (3) is 22·8 per cent. of the heat which the snbstance evolves on explosion.

Trinitrotoluene evolves on detonation a much lower quantity of heat (4) than glyceryl trinitrate (1), and, moreover, the heat evolved is a much smaller proportion of that evolved by the corresponding system of elements (5) than in the case of glyceryl trinitrate. Such a system would evolve 147 per cent. more heat than is produced by the simple explosive, as against 64 per cent. for glyceryl nitrate. In trinitrotoluene, however, we have a substance in which the deficit of oxygen is so great that 1 kilo. would require 0·74 kilo. of additional oxygen for its complete combustion. Trinitrotoluene suffers, therefore, from its uncompensated character as regards the oxygen it carries for the combustion of its elements. The extent to which it suffers from the lost energy involved in its formation from the elements may be gathered from the table, where the heat evolved from combustion of its elements (7) is set down in comparison with the heat experimentally found when trinitrotoluene is burned in oxygen (6). In this case, the heat due to the combustion of the elements, together with their necessary oxygen, is only 1·3 per cent. more than that which is evolved by a system composed of trinitrotoluene and its necessary oxygen. It will be seen, therefore, that the lower total energy associated with trinitrotoluene is due, for the most part, to its want of oxygen, but that when the compensated explosive, glyceryl trinitrate (1), and the compensated system of trinitrotoluene with the oxygen it requires for complete combustion (6), are each of them compared with the heat evolved by the systems made up of their carbon and hydrogen and necessary oxygen, (2) and (5), the loss suffered by trinitrotoluene is much less than that by glyceryl

trinitrate in the proportion of about one to four. This is due to the lower heat of formation from the elements, and especially to the much smaller wastage of energy by methylation as compared with hydroxylation. Thus, whilst the heat of detonation of trinitrotoluene is much less than that of glyceryl trinitrate, it has been formed with much less wastage of energy.

When an explosive mixture is made with an oxygen-bearing salt, such as ammonium nitrate, in proportions for the complete oxidation of all the combustible elements of the system, the heat evolved, whilst greater than that given by trinitrotoluene itself, is still less than half of what the combustible elements in trinitrotoluene would give if they underwent combustion in oxygen. This is, of course, again due to the adverse effect of the high heat of formation of ammonium nitrate.

Generally, it can be said, in comparing nitric esters with nitro-compounds, that whilst a large proportion of oxygen can be readily introduced into the molecule of nitric esters by means of the $O{\cdot}NO_2$-group, they have the disadvantage of a higher heat of formation, as the heat which is lost in the combination of carbon and hydrogen is more in the case of the paraffins than in the case of the aromatic hydrocarbons, and, further, much heat is wasted in hydroxylation.

From the point of view of total heat energy, then, an advantage rests with explosives in which the oxygen is supplied either in the uncombined form, as in the liquid air explosives, or by a compound of which the heat of formation is small. Of this type are explosives in which petrol or nitrobenzene, for example, is used in conjunction with nitrogen peroxide, the heat of formation of which from its elements is low (1·7 kg. cal. per mol.), loss of energy by the formation of a compound between combustible and oxygen-bearing substance being in this case avoided. Thus 1 kilo. of a mixture of nitrogen peroxide and nitrobenzene, arranged for complete combustion, would give 1790 kg. cal. (water gaseous), or 21 per cent. more than glyceryl trinitrate.

Such mixtures, therefore, have the advantages of being readily arranged for complete combustion, and of being constituted so that there is little loss in the formation of their components. They are consequently very powerful, and may also be very violent, but have the practical drawbacks associated with the handling of volatile liquids.

It is now of interest to follow the effect of the introduction of nitro- and other groups. The heats of combustion, from which are deduced the heats of formation, have been the subject of study at the Research Department, Woolwich, and an account of the work

and of the values for the most important nitro-derivatives of benzene, toluene, phenol, and methylaniline is being published in the names of Messrs. Garner and Abernethy.

It has been found that there is no constant difference produced by the introduction of a nitro-group or of successive nitro-groups into the benzene nucleus, but that the internal energy of the molecule, as shown by its heat of formation, varies with the position of the entering nitro-group with reference to other nitro-groups and to other substituting groups. Generally, it is found that the molecule has the greatest strain—lowest heat of formation—in which the nitro-groups are adjacent to one another, and this strain is reflected in the lower chemical stability and the greater sensitiveness to impact of those members of the series possessing the lower heat of formation. The heats of formation of the isomerides of trinitrotoluene range from $+10{\cdot}2$ kg. cal. per mol. for the 2:4:6- to $-2{\cdot}0$ (carbon–diamond) for the 2:3:4-compound, and all these isomerides give off more gas on heating at a given temperature, and explode by the application of a blow of less energy, than the symmetrical substance. As a further example, 1:2:4-trinitrobenzene has been found to be more sensitive and less chemically stable than the symmetrical 1:3:5-isomeride. This will be further alluded to in the portion of this paper which deals with chemical stability.

The comparatively low heat of formation of the compounds in which adjacent nitro-groups occur will be noted in connexion with the well-known difficulty of preparing substances in which there are two nitro-groups in the ortho-position to one another.

The introduction of nitro-groups in the parent substances of the four series mentioned above produces compounds which, at least after three groups have entered, have for the most part still a heat of formation greater than that of the original substance, but from results obtained so far, it appears to require four nitro-groups to bring the heat of formation markedly below that of the parent substance. Thus the heats of formation of benzene, toluene, phenol, and methylaniline, compared with those of their symmetrical trinitro-derivatives, are respectively $-10{\cdot}6$ and $+4{\cdot}9$, $-3{\cdot}8$ and $+10{\cdot}2$, $+33{\cdot}2$ and $+47{\cdot}1$, and $-7{\cdot}9$ and $+7{\cdot}1$ kg. cal. per mol. (carbon–diamond). A fourth group (in the side-chain) in the case of trinitrophenylmethylnitroamine brings the heat of formation to $-11{\cdot}4$, which is below that of methylaniline. It will be seen, also, that whilst the introduction of a hydroxyl group is productive of a considerable increase in the heat of formation, oxygen then be added in the form of nitro-groups without any serious loss s.

degradation in the energy of the molecule, and this is of importance in explaining the explosive character of nitro-compounds.

In another type of explosives, such as are used as initiators, which require to be of a very sensitive character, a very low or negative heat of formation reflects their great internal strain. Examples of these are mercury fulminate, which absorbs 62·9 kg. cal. per mol. in its formation from its elements (Berthelot), and lead azide, which absorbs 105 kg. cal. per mol. (Martin), and is characterised by the strain resulting from the rings containing three nitrogen atoms.

The work on the heat of formation of the benzenoid substances has been more recently the subject of special study, on account of its bearing on the properties of explosives used on the largest scale, and so has been more fully treated in the foregoing remarks.

The heat of formation of all explosive substances is of fundamental importance in affording data for the study of their chemical characteristics and the evaluation of their explosive properties.

(2) *Heat of Explosion and Gases Evolved*.—The methods of determination of the heat of explosion and of estimating the volume and nature of the gases have hitherto been unsatisfactory so far as high explosives are concerned. For propellants the problem is simpler, as the pressures developed in the apparatus, even when they simulate those occurring in guns, are comparatively small, for example, not exceeding 25 tons per square inch. Methods have been described for high explosives, but in these the proportion of explosive to vacuous space has frequently been too small, thus introducing a condition unrepresentative of practice, or when this is avoided by the more practical method of detonating the explosive in its own volume enclosed in some resisting envelope, gases only, and not calorimetric values, have hitherto been reported (Poppenberg and Stephan, *Zeitsch. ges. Schiess- u. Sprengstoffw.*, 1910, **5**, 291).

The difficulties to be overcome with high explosives are very great when it is considered that the pressures developed locally are of the order of 300 tons per square inch. Whilst a final form of the calorimetric bomb for measuring the heat of detonation of high explosives has not yet been reached, it has been found possible in a bomb of moderate capacity to measure the heat developed from the detonation of explosives pressed to a high density in containers representative of practical conditions. The difficulties of designing a bomb which withstands the blow without leakage have been overcome, and the gaseous products of detonation can be measured and analysed. The explosive, compressed to any

desired density, is retained in a stout envelope, usually of steel, and complete detonation is secured by applying to it an intense impulse from a fulminate or lead azide detonator, retained, as has been found necessary, in steel of considerable thickness. The detonator is fired electrically by an insulated connexion passing through the obturated plug of the bomb. The bomb is immersed in a calorimeter of the type described for the propellant bomb (Robertson, *Proc. Roy. Soc.*, 1907, [*A*], **79**, 320), and the gases collected in the gas holder described in that paper, water, ammonia, and hydrocyanic acid being also estimated.

Some of the values that have been obtained for the heat evolved by the detonation of simple explosives in this bomb are given in the following table, and the values for guncotton and for glyceryl trinitrate are added for comparison.

TABLE II.

Heat and Gases on Detonation.

Explosive detonated at density = 1·3.	Calories per gram (water gaseous).	Total gases, c.c. per gram.
m-Dinitrobenzene	820	727
Trinitrobenzene	940	820
Trinitrotoluene	924	728
Trinitrophenol	914	744
Trinitrophenylmethylnitroamine	1090	794
Guncotton (Nitrogen, 13 per cent.)	982	875
Glyceryl trinitrate	1478	713 (Berthelot)

The comparatively high heat value for dinitrobenzene is of interest when it is remembered that this is not far from the value of the heat energy contained in some military propellants, but it was left to this war to demonstrate that a compound with only two nitro-groups in the benzene ring, and requiring an addition of 95 per cent. of its own weight of oxygen for its complete combustion, could be used without admixture as a high explosive for shell. Its other constants, which reflect its properties and possibilities, will be referred to below.

The values obtained for trinitrotoluene and for picric acid differ from those reported by Poppenberg, who gives 641 and 793 calories per gram respectively. The new results have been obtained, as has been said, by detonating the explosives enclosed in a steel envelope at a density of loading in the envelope of 1·3, and they agree with results calculated from gas analyses from larger quantities, also confined in steel envelopes and detonated in a large, exhausted vessel.

The heat values obtained for trinitrotoluene and picric acid are

interesting in that the difference in heat energy given by the two explosives is small, although trinitrotoluene requires 74 per cent. of its own weight of oxygen for its complete combustion, whilst picric acid requires only 45 per cent. This considerable disadvantage in the case of trinitrotoluene is, however, counterbalanced by the lower heat of formation of 2 : 4 : 6-trinitrotoluene (10·2 kg. cal.) (carbon–diamond) as compared with trinitrophenol (47·1 kg. cal. per mol.), or a difference of about 160 gram-cal. per gram in favour of trinitrotoluene. This difference is due to the energy lost by hydroxylation as compared with methylation of the benzene, as is shown by the molecular heats of formation (carbon–diamond), −10·6 kg. cal. for benzene, −3·8 kg. cal. for toluene, and +33·2 kg. cal. for phenol.

The sometimes alleged inferiority of trinitrotoluene to picric acid as an explosive therefore receives little support when total energies of the respective substances are considered. There is, however, a somewhat higher quantity of gas from unit weight of picric acid, as might be expected from its higher oxygen content.

It will be observed that trinitrophenylmethylnitroamine has a much higher heat of detonation than trinitrotoluene or trinitrophenol, and this is in accordance with all the properties of this substance, which is used as an energetic intermediary between the detonator and a main explosive.

It will also be seen that the total heat energy of all these explosives falls considerably short of that of glyceryl trinitrate, in spite of the high heat of formation of that substance, this being due to the difficulty in getting a stable nitro-compound containing enough oxygen in the form of nitro-groups to oxidise the combustible elements of the molecule.

The technique of the calorimetry of high explosives is being further developed in the direction of using charges of considerably greater magnitude, so that corrections due to the presence of initial detonant will be correspondingly reduced, and less sensitive explosives detonated with certainty.

(3) *Chemical Stability.*—The chemical stability of explosive compounds can be determined by the rate at which they undergo decomposition, an elevated temperature being required to bring this to a measurable degree for most of the explosives used in practice. In one of the methods considered, the explosive is caused to decompose either in a stream of inert gas, where the products are determined volumetrically (Will, *Zeitsch. angew. Chem.*, 1901, **14**, 743), or spectroscopically (Robertson and Napper, T., 1907, **91**, 764; Robertson, T., 1909, **95**, 1241). In another, the decomposition is followed by observing the rise in pressure of

the gases given off in a vacuum, as in the method devised by Farmer (T., 1920, **117**, 1432), which is applied to most of the more stable nitro-compounds. In this case, the explosive is contained in a tube connected with a mercury manometer, the tube and it's contents being kept at a constant temperature in a specially fitted bath.

Explosives appear to be continuously decomposing at a rate which is a function of the temperature, but that rate is slow at ordinary temperatures in the case of explosives capable of practical employment. Thus trinitrotoluene at 140° gives off gas extremely slowly. The cellulose nitrates are less stable than trinitrotoluene, and glyceryl trinitrate still less stable. At a temperature as low as 55°, the evolution of nitrogen peroxide from *5 grams of glyceryl trinitrate can be observed in a 2-metre tube* by means of the spectroscope.

This intrinsic decomposition proceeds even when the explosive is dry; but hydrolysis may be superadded in the presence of moisture, and both of these types of reaction are accelerated by the products of decomposition. Thus nitrogen peroxide, a product of the degradation of cellulose nitrates and of glyceryl trinitrate, rapidly accelerates the intrinsic decomposition of these esters, possibly on account of its strongly oxidising properties, whilst the acceleration of their hydrolysis is due to its acid-forming properties.

It has been shown (*loc. cit.*) that retention of nitrogen peroxide in the presence of cellulose nitrate undergoing regulated decomposition induces an acceleration. Thus it was shown that the higher the concentration of nitrogen peroxide existing in the gases in contact with the heated cellulose nitrate, the greater was the amount by which the rate of decomposition exceeded the minimum rate characteristic of the completely purified explosive when it is caused to decompose with simultaneous removal of its volatile products. Even a nitro-compound like picric acid, which is very much more stable, has been found to undergo an accelerated decomposition in the presence of nitrogen peroxide, although, of course, at a temperature much above that required for this effect with cellulose nitrates.

The slow decomposition which occurs during warm storage for the most part results in the formation of less simple products than those developed on detonation, and the rate of their evolution is influenced by the chemical constitution and composition of the explosive, as well as by the following factors:

(*a*) The quantity of heat evolved by the decomposition of the

explosive; this has a positive value, but less than the heat evolved on detonation.

(*b*) The temperature of storage; the rate of decomposition is about doubled for a rise of 5°.

(*c*) The conductivity of the explosive for heat and its specific heat, especially where large masses are involved, since these properties determine the extent to which heat is retained in the central portions of the mass; explosives, like organic materials in general, are bad conductors of heat, the conductivity of many having been found to be about the same as that of porcelain.

(*d*) The action of the products of decomposition on the unchanged material; this includes such acceleration as that caused by nitrogen peroxide, mentioned above.

(*e*) The physical condition of the explosive; this influences the retention or diffusion, and possible elimination, of disturbing impurities.

(*f*) The presence of foreign substances; these may either exert a powerful accelerative influence, or, on the contrary, may reduce the rate of decomposition by combining with products which would otherwise accelerate.

Most explosive substances can be induced to undergo a regulated decomposition if care be taken steadily to withdraw, by suitable means, the heat evolved by the exothermic reaction and those gaseous products which act as catalysts in accelerating decomposition, for example, by leading a stream of gas through the system or by conducting the operation in a vacuum, or by permitting the environment to absorb the heat.

The temperature-coefficients of such decompositions lie between 1·7 and 2·3 for 5°. This is greater than for many other types of chemical reactions, for which the rate is approximately doubled for a rise of 10°. It is important that this temperature-coefficient should be known throughout a range extending from the storage temperature, on the one hand, to a higher one at which the rate of decomposition can be measured in a reasonably short space of time. Examples of temperature-coefficients which provide this link between warm storage temperatures and a much higher temperature are included, among others, in table III (p. 12).

These temperature-coefficients have been determined by various methods of experiment.

The decomposition over the longest range quoted is for glyceryl trinitrate, the method used being that described previously (Robertson, T., 1909, **95**, 1241). When that paper was written, 90° was the lowest temperature at which decomposition had been

TABLE III.

Temperature-coefficients.

	Temp.-coeff. for 5°.	Limits of experiment.
Mercury fulminate	1·7	50—80°
Glyceryl trinitrate	2·2	60—135°
Guncotton	1·9	125—150°
Tetryl	1·95	100—115°
Picric acid	2·3	140—180°
2 : 4 : 6-Trinitrotoluene	1·85	140—180°
2 : 4 : 5-Trinitrotoluene	1·8	120—140°
do.	1·8	140—180°

observed. Since then, in conjunction with W. S. Simpson, quantitative results have been obtained by the same spectroscopic method down to 60°. Certain refinements were introduced, such as distribution of the glyceryl trinitrate, present necessarily in larger quantities, over silica wool, and the use of a quartz observation tube lengthened to 2 metres. The over-all temperature-coefficient obtained between 60° and 135° was found to be 2·2 for 5°, and was fairly constant throughout this range.

Whilst there is thus no very great difference in the rate of increase in the velocity of decomposition with rise in temperature among explosives of widely different types, their resistance at the same temperature varies enormously.

Examples are given in table IV (p. 13) of the rates of decomposition of a number of explosives. An attempt has been made to institute a comparison among these rates by quoting the volume of gas evolved from 1 kilo. of the explosive per hour (after forty hours' heating) at 140°, either experimentally determined, or deduced from the results obtained at the nearest temperature at which the experiment was carried out.

The figures quoted are the rates of gas evolution at an early stage in the decomposition, before the usual marked acceleration caused by the products of decomposition sets in. This acceleration differs greatly in different explosives, and this has to be taken into consideration when questions involving safety are concerned.

Considering, in the first place, the gas evolved from those aromatic nitro-compounds given in the table, it is not until a trinitro-derivative is reached that a measurable gas evolution is obtained. Of these, the most stable is 1 : 3 : 5-trinitrobenzene, which gives off only a trace of gas when heated for many hours even at the high temperature of 180°, or nearly 60° above its melting point.

Table IV.

Stability of Explosives.

Rates of gas evolution in c.c. per hour after forty hours from 1 kilo. of explosive.

Explosive.	80°.	120°.	140°.	160°.	180°.
m-Dinitrobenzene	—	—	0*.	—	—
2 : 4-Dinitroaniline	—	—	0*	—	—
1 : 3 : 5-Trinitrobenzene	—	—	0*	—	0·05
2 : 4 : 6-Trinitromesitylene	—	—	*0·003*	—	*8·4*
2 : 4 : 6-Trinitro-*m*-xylene	—	—	0·5	8·0	—
2 : 4 : 6-Trinitrophenol	—	—	0·6	—	—
2 : 4 : 6-Trinitroaniline	—	—	4	—	—
1 : 2 : 4-Trinitrobenzene	—	—	8	—	—
2 : 4 : 6-Trinitrotoluene	—	—	9	—	—
2 : 4 : 6-Trinitro-*m*-cresol	—	—	10	—	—
2 : 3 : 4-Trinitrotoluene	—	—	13	—	—
2 : 3 : 5-Trinitrotoluene	—	1·5	[24]	—	—
2 : 4 : 5-Trinitrotoluene	—	—	32	—	—
2 : 4 : 6-Trinitroanisole	—	—	32	—	—
2 : 4 : 6-Trinitrophenylmethylnitroamine	—	8	[128]	—	—
2 : 3 : 4 : 6-Tetranitroaniline	—	18	[288]	—	—
3 : 4 : 5-Trinitrotoluene	—	22	[352]	—	—
2 : 4 : 6-Trinitro-3-hydroxyphenylmethylnitroamine	—	23	[370]	—	—
Cellulose nitrate (N_2=13%)	—	{at 135° 2500}	[5000]	—	—
Glyceryl trinitrate	—	{at 115° 1660}	[86.000]	—	—
Lead azide	—	—	—	—	40
Mercury fulminate	2·5	—	—	—	—

* Not measurable at 140°.

The influence of the successive introduction into the ring of nitro-groups is shown in the series dinitroaniline, trinitroaniline, and tetranitroaniline, where the fourth group induces a great increase in the gas evolution. In the case of some compounds, the introduction into the ring of a fourth nitro-group leads to an even more marked instability.

Examination of the products of decomposition of trinitrotoluene shows that they are very complex, but they contain a substance resembling the transformation product of uncertain constitution and lower stability, that is associated with the action of alkalis and of light. It is of interest in this connexion that the resistance to decomposition by heating of the mono-, di-, and tri-methyl derivatives of trinitrobenzene runs in line with that of their resistance to the formation of this transformation product by alkalis and by light.

Hydroxylation, as shown in the simpler series of trinitrobenzene and trinitrophenol, and of trinitrotoluene and trinitrocresol,

increases the gas evolution only to a slight extent. It has a more marked influence, however, in trinitrophenylmethylnitroamine, due, apparently, to an acceleration of hydrolysis, a feature which will be treated of later.

Examples are given of the arrangement of nitro-groups in the benzene ring. It will be seen that 1:2:4-trinitrobenzene is less stable than the 1:3:5-compound, and in the case of the isomerides of trinitrotoluene, the 2:4:6-compound is the most stable of all.

On reviewing the order of stability of the compounds in the table generally, it is of interest to note that their decreasing resistance runs in line with the ease with which they can be hydrolysed. Thus, in the case of the two last-mentioned series, the mobile character of one of the nitro-groups in the unsymmetrical trinitro-derivatives is well known. Again, when trinitrophenylmethylnitroamine is hydrolysed, methylamine and picric acid are among the products, and picric acid is found to accelerate the decomposition of the substance (Farmer, T., 1920, **117**, 1603). Picric acid is also found among its products of decomposition in the stability test, and it is no doubt due to the acid properties conferred on trinitrohydroxyphenylmethylnitroamine by the hydroxyl group that that substance possesses a lower stability than trinitrophenylmethylnitroamine.

Trinitroanisole, which partakes of the character of an ester, and is readily hydrolysed, is found to undergo a more rapid decomposition than picric acid.

Of the others, which are the more stable, as shown by their low gas evolution, indifference to hydrolysis is a characteristic feature.

It would thus appear from these indications of lower stability, in conjunction with greater hydrolysability, that the water pro*duced by interaction of the oxygen of the nitro-groups and* hydrogen in the side-chains or in the ring, may be a condition for *greater chemical action, as shown by the volume of gas evolved.*

Compared with the nitro-compounds in the table, the resistance to heat of the nitric esters, cellulose nitrate, and glyceryl trinitrate is of a much lower order.

This is thought to be due, perhaps, less to inherent instability in these nitric esters than to their ready hydrolysis by traces of water formed during the decomposition and the vigorous interaction of the products of hydrolysis.

In addition to considering the effect of the chemical nature of these substances as regards their rate of decomposition, however, it is necessary to take into account their physical condition, since their stability is greatly influenced by the state of aggregation.

Thus the decomposition of trinitrophenylmethylnitroamine was measured a few degrees below its melting point (129·1°) by the method of observing the rate of disengagement of nitrogen in a stream of inert gas, and the values obtained were extrapolated to 135°, a few degrees over its melting point. The disengagement at 135°, when it was actually liquid, was also determined by the same method, when it was found that the rate of decomposition of the liquid substance was fourteen times that which the solid would have had at the same temperature.

When the same explosive was brought into the liquid condition by adding an inert nitro-compound, it was found that it gave off in a vacuum about fifty times as much gas at the same temperature as it did when in the solid condition (Farmer, T., 1920, **117**, 1603).

In the preceding table, the figures of gas evolution are referred to the liquid condition, for the sake of obtaining strict comparisons. To those compounds the melting points of which lay above the temperature of experiment, sufficient of an inert nitro-compound was added to render them liquid during the period of heating.

The increase in the rate of decomposition of an explosive in the liquid as compared with that in the solid state is doubtless connected with the greater mobility of the molecules in the liquid condition.

There are reasons for supposing that the decomposition of solid explosives takes place at the surface of the particles. Thus, Hinshelwood and Bowen (*Phil. Mag.*, 1920, [vi], **40**, 569) have shown that the rate of gas evolution from solids which give off gas is conditioned by the amount of surface exposed. In working with mercury fulminate, W. L. Turner has shown that the degradation of fulminate on heating, although it does not give rise to a change in the external form of the crystals, can be followed by means of the difference in optical properties between unchanged fulminate and the products of decomposition. After fulminate has been heated until a considerable quantity of gas has been set free, the crystals present the appearance of a central, unchanged nucleus surrounded by decomposition products.

(4) *Sensitiveness to Shock.*—All explosives are more or less readily brought to detonation by a mechanical shock. The investigation of the degree of sensitiveness exhibited is important, as the sensitiveness largely determines the applications to which explosives can be put, and also the character of the precautions necessary to ensure safe manufacture and handling.

The explosive is tested for sensitiveness to two distinct types of

blow: direct impact and friction. The measurement of sensitiveness to direct impact admits of greater quantification, and I propose to deal only with it on this occasion.

The determination of sensitiveness to a blow is generally carried out in a drop-weight machine. The experiments are fraught with many difficulties, and few of the published data can be regarded as trustworthy.

The difficulties are chiefly due to the complex effect which the blow has on the explosive, to the great labour and expense in maintaining the striking surfaces constant throughout the work, and to the interpretation of the results obtained, which has for the most part depended on qnalitative personal views.

These difficulties have to a great extent been overcome by the use of a falling weight instrument worked out by Dr. Rotter, of the Research Department, Woolwich. By this method, it is possible to reproduce accurately the disposition of the explosive, whilst the surfaces between which it is struck are carefully standardised by comparing the behaviour of the explosive under investigation with that of a standard explosive. The results of the blow are evaluated, not by personal observations of sound, flash, or by the imperfect guide of assessing the quantity of scattered residues, but by a quantitative measurement of the gas produced at the different heights of fall when the blow delivered has sufficient energy to cause decomposition of the explosive and gas to be evolved.

The results are given in comparison with a standard explosive according to the type under investigation, the usual standards being picric acid, gunpowder, and mercury fulminate. The sensitiveness is expressed in ratios, known as "figures of insensitiveness," which express the relative energies of the blows required to produce explosions of equal degrees of completeness throughout the scale from incipient to complete detonation. A table is appended giviug some typical results. Picric acid is taken as 100, and the lower numbers refer to explosives of greater sensitiveness.

The range of sensitiveness is very great. At the one end lie the haloids of nitrogen, which can scarcely be handled without exploding, whilst at the other end are the aromatic nitro-hydrocarbons, which are brought to detonation only by a very heavy blow.

The sensitiveness of explosives to mechanical shock is undoubtedly closely related to their chemical constitution, but the relationships are frequently masked by differences in physical

character, which greatly modify the pressure developed by a blow of given intensity.

Theoretically, all explosives are decomposing very slowly, with evolution of heat, at the ordinary temperature. The energy which must be supplied to raise the rate of decomposition to explosion is a measure of the sensitiveness. It follows that all explosives increase in sensitiveness with rise in temperature. The quantity of heat liberated by the explosive on decomposition plays an important part in raising the rate of reaction to that of explosion, and it is found that, in similarly constituted substances, the higher the heat of explosion the less is the quantity of energy that need be added.

A good example of this is glyceryl trinitrate, which exhibits great sensitiveness when struck between two hard substances, but it is also exemplified in all the series of nitro-compounds into which nitro-groups are successively introduced. Further, in nitro-compounds containing the same number of nitro-groups, but differing in heat of formation, in consequence of the different arrangement of the nitro-groups, it is found that those are the more sensitive which have the lowest heat of formation, that is, presuming a similar metamorphosis to take place on explosion.

The following general observations can be made as to the relation of chemical constitution to sensitiveness.

Aromatic nitro-componnds with one or two nitro-groups in the ring are very insensitive. The effect of introducing more nitro-groups is successively to increase the sensitiveness. This is illustrated by the series of nitroanilines shown in table V (p. 18).

In all cases, increasing sensitiveness is associated with either some peculiarity of constitntional arrangement in the explosive or with higher heat of explosion due to the importation of more oxygen into it, so as to render the substance more nearly balanced for complete combustion. The influence of the position of nitro-groups in the case of isomerides of a substance like trinitrotoluene, for example, is, of course, of a much smaller order than that associated with the highly strained structure of compounds like fulminate and lead azide, as shown by their strongly endothermic character.

(5) *Rate of Detonation.*—The rates of detonation have, for the most part, been determined by the Dautriche method, a column of the explosive under standardised conditions of confinement being contained in a steel tube of 1·2 inches internal diameter and 0·1 inch wall, and detonated by a terminal charge of 50 grams of trinitrophenylmethylnitroamine.

TABLE V.

Sensitiveness of Explosives.

Figures of Insensitiveness (Picric Acid = 100).

	Figure of insensitiveness to impact.
Initial detonants:	
Mercury fulminate	10
Lead azide	20
Nitric esters:	
Glyceryl trinitrate	13
Nitrocellulose	23
Nitro-compounds:	
p-Nitroaniline	over 120
2 : 4-Dinitroaniline	over 120
2 : 4 : 6-Trinitroaniline	111
2 : 3 : 4 : 6-*Tetranitroaniline*	86
1 : 3 : 5-Trinitrobenzene	107
2 : 4 : 6-Trinitrotoluene	115
2 : 4 : 6-Trinitro-*m*-xylene	over 120
1 : 3 : 5-Trinitrobenzene	106
2 : 4 : 6-Trinitrophenol	100
2 : 4 : 6-Trinitrotoluene	115
2 : 4 : 6-Trinitro-*m*-cresol	101
2 : 4 : 6-Trinitrophenylmethylnitroamine	70
2 : 4 : 6-Trinitro-3-hydroxyphenylmethylnitroamine	56
2 : 4 : 6-Trinitrotoluene	115
2 : 3 : 4 ,,	92
2 : 4 : 5 ,,	102
3 : 4 : 5 ,,	102
2 : 3 : 5 ,,	108
2 : 3 : 6 ,,	111

The method of Dautriche is well known, and need be only shortly described. The detonation wave, passing along the column of explosive confined in its steel tube, causes detonators fixed to the ends of a loop of the detonating lead-covered fuse to start a wave of detonation in the fuse. These detonators are separated by a known distance in the explosive, and the meeting point of the two approaching waves is displaced from the real centre of the loop by an amount from which, knowing the rate of detonation of the fuse and the distance apart of its initiating detonators, the rate of detonation can be calculated. The meeting point of the waves is recorded as a sharp, transverse line marked on a lead plate, on which the fuse is laid. The lead-covered detonating fuse for this work was standardised in 3-metre lengths by the Mettegang apparatus in order to obtain its rate of detonation.

The results given by some of the explosives mentioned in other connexions in this paper are as follows.

TABLE VI.

Rates of Detonation.

Explosive.	Density of loading.	Metres per second.
Trinitrophenylmethylnitroamine	1·63	7520
Guncotton (dry)	1·2	7300
Trinitrophenol	1·63	7250
Trinitrotoluene	1·57	6950
Trinitroxylene	1·51	6600
m-Dinitrobenzene	1·56	6100
Mercury fulminate	loose	3000

The rate of detonation of an explosive is one of the chief characteristics which serve as an indication of its violence or shattering effect. Whilst the calorific value of an explosive gives the total possible energy which an explosive can exert, the rate of detonation is the rate at which the energy is evolved, and is of great importance as regards the effect produced. The effect of rate of detonation is well marked in the result of the pressure-bar tests, next to be described, a high rate giving a large value for the instantaneous maximum pressure, whilst at a similar density of loading with a lower rate, a lower pressure is obtained, although sometimes with a higher total blow.

The quantity of heat energy available seems to be related to the rate of its expenditure. Thus it will be seen from the table that the rate of detonation runs in line with the heat of explosion as given in an earlier section, and therefore, like this property, is to a large extent dependent on molecular structure.

(6) *Pressure Developed.*—For determining the degree of violence developed by an explosive, the methods hitherto in use have been inadequate. This has been due to insufficient weight being attached to the need for obtaining quantitative measurements, which have a definite physical meaning. Moreover, the importance of maintaining uniform and controlled conditions of such factors as density of loading and degree of confinement of the charge, have not always been sufficiently realised.

An advance in the direction of obtaining quantitative measurements of the pressures developed by explosives over a small measurable interval of time, which is a measure of the violence they exhibit, has been made possible by the application of the method of determining the pressure of a blow put forward by the late Prof. Bertram Hopkinson (*Phil. Trans.*, 1914, [*A*], **213**, 437). By this method, valuable results have been obtained, which

have thrown light on the properties of explosives and enabled choice to be made among them for specific purposes, such as to initiate detonation in other explosives, and it has proved to be of theoretical importance in obtaining insight into the properties of detonation waves. It has also been fruitful in the investigation of the design of mechanisms, such as detonators, fuses, and gaines,* since it affords definite and immediate information on the essential feature of such components, namely, the violence of the blow that they deliver. As the method developed, its usefulness as a check on supply was appreciated, and instruments were designed for control of the quality of such stores as have been mentioned.

The application of Hopkinson's principle to this wider field of research, and the design of a variety of instruments for the purposes mentioned above, were carried out at the Research Department, Woolwich, by Mr. H. Quinney, formerly Hopkinson's assistant, and a number of other physicists.

The principle on which the determination of the pressure is based depends on the fact that when a charge is fired against the end of a cylindrical steel bar ballistically suspended, a wave of compression travels along the bar and is reflected at the far end as a wave of tension. To investigate the properties of the wave, a short length of the end of the bar farthest from the delivered blow is cut off and the faces surfaced, the short piece (known as the time-piece) being caused to adhere closely to the bar, usually by a film of vaseline. The compression wave travels unchanged through the joint into the time-piece, but the film is unable to transmit a tension. Hence when the amplitude of the reflected tension wave reaching the joint becomes greater than that of the oncoming compression wave, the time-piece is projected off the end of the shaft with a momentum which depends on the pressure exerted by the explosive and the time taken by the wave to traverse the length of the time-piece. This momentum is measured by catching the time-piece in a ballistic pendulum, and the velocity of the propagation of the wave through steel being known, the mean pressure exerted during an extremely small time interval can be calculated. The principle thus essentially depends on the experimental separation of this momentum into its two factors of pressure and time. By the use in succession of time-pieces of different lengths, it is possible to make an approximation to the maximum pressure developed, and to get values for the mean pressure over various time intervals, and the time taken for the

* A term which has become common in connexion with explosive mechanisms, as signifying a tube containing an intermediary detonating explosive or system (Fr. *gaine*, a sheath).

pressure wave to reach its maximum amplitude and fall to nothing. The time interval over which the mean maximum pressure is normally measured is a two-hundred thousandth of a second, and the pressures developed in these experiments reach a magnitude of hundreds of tons per square inch. To protect the end of the bar against the application of such stresses, which no terrestrial substance would withstand, a standardised pellet of material, which is scattered on the explosion, is interposed between the explosive and the end of the bar. This has the effect of degrading the blow to a known extent. Values for pressure, quoted later, are thus

TABLE VII.

Results on Pressure Bar.

Explosive.	Thickness of steel envelope.	Density of loading.	Pressure in tons per sq. inch in 0·5 × 10^{-5} second.*	Density of loading.	Pressure.	Density of loading.	Pressure.
Tetryl	None (paper).	—	14·2	1·45	—	1·55	—
	1/16"	1·3	31·7	1·45	34·5	1·55	35·1
	1/4"	1·2	51·2	1·45	55·9	1·55	57·8
	1/2"	1·2	62·3	1·45	—	—	—
T.N.T.......	None (paper).	1·2	13·2	—	—	—	—
	1/16"	1·2	—	—	—	1·55 (cast).	31·1
	1/4"	1·2	46·1	—	—	1·55 (cast).	55·0
	1/2"	1·2	56·2	—	—	—	—
Trinitrophenol	None (paper).	1·2	11·8	—	—	—	—
	1/4"	1·2	43·3	—	—	1·6 (cast).	54
	1/2"	1·2	50·2	—	—	—	—
Trinitro-*m*-xylene ...	1/4"	1·2	41·5	1·45	43·7	—	—
m-Dinitrobenzene...	1/4"	1·2	32·9	—	—	—	—
2 : 4-Dinitrotoluene ...	1/4"	1·2	31·1	—	—	—	—
Dinitronaphthalene (crude) ...	1/4"	1·2	14·1	—	—	—	—
Nitrobenzene... (liquid)	1/4"	1·18	4·0	—	—	—	—
Nitrobenzene... (solid)	1/4"	1·2	3·8	—	—	—	—
Benzene...... (solid)	1/4"	1·0	3·8	—	—	—	—

* With constant pellet interposed.

always to be taken as an approximately known fraction of the actual pressure.

By addition of the momentum of the time-piece to that of the bar, which is readily measured by taking the amplitude of its first swing, a value for the total blow delivered to the end of the bar can be expressed in units of momentum without reference to the *duration of the blow*.

A large amount of work has been done by this method, but it is possible only to refer to a few of the results.

Some examples may be given of the differences brought out among explosives as regards their comparative violence, and the values (table VII, p. 21) at the same time exhibit some other features. The initiating system in all cases was an intense one, and was constant throughout.

Some description may be given of the character of the information that has been obtained in the investigations with the pressure bar.

In carrying out these experiments, it was found necessary to pay the greatest attention to maintaining as constant as possible the density of loading and the thickness of the containing envelope before it was possible to make any deductions.

In all the cases quoted, higher pressures occur at the higher *densities of loading, but this result* is obtained with the more heavily compressed explosives only when the initiating impulse is sufficiently intense to overcome their insensitiveness to detonation.

From the values given in the table, the important exaltation of effect due to the confinement of the explosive is very clear.

In the case of simple explosives, the measured pressures developed appear to be dependent on the rate of detonation, the heat of explosion, the volume of gas produced, and the density of loading, but further data under standard conditions are required before the effects due to each of these can be ascertained.

By retaining a constant system of initiating impulse, it is possible by this method to determine the sensitiveness of explosives in responding to a detonative blow. Explosives at high densities of loading respond with more difficulty, and especially when lightly confined.

In the case of mixtures, intimacy of contact of the components, *obtained, for example, by prolonged incorporation of the* ingredients, has also been proved to increase the pressures developed, and to counteract the fall in pressure that occurs with less well-incorporated mixtures when they are heavily compressed and initiated with only a moderate impulse.

Comparing, next, some of the different types of explosives given

in the table as to the pressures they develop, by taking the values obtained in an envelope of $\frac{1}{4}$-inch steel wall, it is seen that the violence of the blow delivered in the same short interval of time (1/200,000th of a second) is greater with tetryl than with picric acid or trinitrotoluene, and this is in line with all the constants of these substances that have so far been considered. It also affords an explanation of the use to which this explosive is put as an energetic intermediary between detonator and less sensitive explosive. There is little to choose between the results given by picric acid and trinitrotoluene, and this also is in agreement with their respective energy contents, and in fair agreement with observations of the fragmentation of steel containers, which, however, on the whole favour picric acid, with its slight advantage in rate of detonation and higher volume of gas.

The entry of another methyl group to form trinitroxylene brings down the violence, but it is still of a high order, and considerably surpasses that of *m*-dinitrobenzene, which contains nearly as much oxygen for its combustion.

Dinitronaphthalene, with its low heat of formation, gives a distinct explosive value, but the application of the intense impulse to which all these explosives were subjected did not cause any disruption of either nitrobenzene or benzene, the effect obtained being only that which was communicated from the initiating system. It does not appear, therefore, as might have been expected from their low heat of formation, that such a blow is capable of breaking up their structure. Dinitronaphthalene, although, from the point of view of oxygen available for its combustion, is little better than a mononitro-derivative of benzene, still appears to have a definite explosive property.

Just as a certain tardiness has been observed for certain explosives in attaining their proper rate of detonation, especially under an inadequate initiation, so also this has been found, especially in the case of liquid explosives, when they are detonated on the pressure-bar. This and many other applications cannot be described within the limits of this paper, but enough has perhaps been said to indicate the importance of the application, and for the purpose of further research the usefulness, of the principle enunciated by the late Prof. Bertram Hopkinson.

Under the headings of the various properties considered, some attempts have been made at correlation with the chemical structure of the explosive compounds. It does not seem possible, however, in our present state of knowledge to connect up all of these properties, which sometimes act in opposite directions.

Certain broad generalisations; of course, appear, chiefly with regard to the inherent energy of the substance influencing such properties as sensitiveness and violence, but chemical stability is more intimately connected with certain aspects of molecular arrangement. There is obviously overlapping in regard to these features of the influence of total energy and special constitutional arrangement, as has been shown in the case of sensitiveness. As will be seen, there is a wide field for work on all these aspects, as also into all the immediate phenomena of detonation.

PART II.

Explosive Properties of the Amatols.

The importance which the amatols ultimately assumed as the only filling for land service shell, for aerial bombs, and other munitions may warrant some sketch of the explosive properties of these mixtures.

Both the pourable mixture, 40/60 amatol (that is, 40 parts by weight of ammonium nitrate and 60 parts of trinitrotoluene), and the 80/20 mixture, were put forward by the Research Department, Woolwich, in March of 1915, as a result of trials which included investigations into their capacity as detonating fillings for shell, their rates of detonation, and their insensitiveness to shock.

The shortage of trinitrotoluene, which was met by the adoption of these mixtures, and especially of 80/20, in which the ingredients are present in nearly the correct proportions for complete combustion, called urgently for their adoption and manufacture on the largest scale, until, finally, the enormous output of 4000 tons a week was reached.

These explosives were of a type which had hitherto not been used for shell-filling in this country, and much had to be learned as to their chemical and explosive properties. These will now be shortly described, following the same order as in the preceding account.

Heat of Formation, Heat of Detonation, and Gases.—In the case of the balanced explosive 80/20 amatol (more nearly 79/21 for complete combustion), since the heats of formation of the constituents and of the products (CO_2 and H_2O) are known, the heat of detonation can be calculated. This heat of detonation has, however, also been determined in the calorimetric bomb for high explosives described above, and is found to be for 80/20 1004 calories per gram (water gaseous), whilst the value calculated from the heats of formation of trinitrotoluene, of ammonium

nitrate, and of the products carbon dioxide and water formed on detonation, is 1019. The agreement is thus fairly good, and is a useful confirmation of the values for the heat of formation of trinitrotoluene and the heat of detonation of the amatol. It is, of course, much more difficult to calculate the calorimetric value of mixtures, such as 40/60 amatol, which are not compensated for combustion, on account of the complexity of the products formed on detonation. The experimental value found for the detonation of 40/60 amatol is 920 cal. per gram (water gaseous).

A fairly good agreement is obtained in the case of 80/20 amatol between the experimental value for total gases evolved from 1 gram of the detonated explosive, 907 c.c., and 894 c.c., the calculated value. Amatol 40/60 gives off 892 c.c. of total gas per gram.

It will be seen that the addition of ammonium nitrate, with its high heat of formation, has no effect on the heat value of trinitrotoluene in 40/60 amatol, although the quantity of gas is increased, but with the theoretical proportion of the components for total combustion, an increase of more than 10 per cent. in total energy is obtained, and, at the same time, the largest volume of gas. The following table gives the experimentally found heat values and gases of these two amatols in comparison with those of trinitrotoluene.

TABLE VIII.

Amatols—Heat and Gases Produced.

	Calories per gram (water gaseous).	Total gases, c.c. per gram.
Trinitrotoluene	924	728
40/60 Amatol..................	920	892
80/20 Amatol..................	1004	907

Stability.—Whilst chemical stability is a necessity in the case of simple explosives which have to withstand a high temperature during either their preparation or their service life, so also with mixtures no less drastic a demand is made on the ingredients, but, in addition, it is necessary that there should be no chemical action between them.

Pure ammonium nitrate and pure trinitrotoluene have little action on one another, even at 120°, but interaction has to be guarded against when certain impurities are present in either of the technically manufactured products, as the concomitants of such interaction are evolution of heat, which may be dangerous, and the generation of gas, which is objectionable in several ways.

The increased mobility associated with the liquid state has been shown in the foregoing to induce a greater rate of decomposition in

simple explosives like tetryl; a similar acceleration occurs in the case of ammonium nitrate if its melting point is depressed by sodium nitrate, for example, so as to form a eutectic, liquid at the temperature of the experiment, when it is found that the rate of evolution of gas is markedly increased in contact with T.N.T. as compared with the evolution from the mixture of that substance and solid, pure ammonium nitrate.

The following gas evolutions show this:

	C.c. from 10 grams of explosive (50/50) in 40 hours.		
	At 100°.	At 110°.	At 120°.
Crude T.N.T. and NH_4NO_3 (pure)	1·2 c.c.	3·7 c.c.	6 c.c.
Crude T.N.T. and NH_4NO_3 containing 8% $NaNO_3$	1·2 c.c.	2·7 c.c.	18 c.c.

It will be seen that it is only when the temperature attains that of the melting point of the eutectic of ammonium nitrate and sodium nitrate, about 120°, that an increased reaction, as shown by the greater gas evolution, supervenes.

The above values are for crude trinitrotoluene, that is, trinitrotoluene containing, as has been shown from thermal analysis of the crude product, a little dinitrotoluene, due to incomplete trinitration, and about 4 per cent. of the isomeric trinitrotoluenes, mainly the 2:3:4 (1·5 per cent.) and 2:4:5 (2·5 per cent.). The reactivity with pure 2:4:6-trinitrotoluene is much less, being for the mixture of the pure ingredients represented by only 2 c.c. of gas under the above conditions at 120°, trinitrotoluene alone giving only about 0·05 c.c.

The gas evolution from the mixture of the pure ingredients of 80/20 amatol is 0·5 c.c. under the same conditions.

As these explosives were now used for the first time in quantit[y] for filling munitions of different kinds, and came into contac[t] with a great variety of metals and materials, their compatibilit[y] with these was the subject of much study, partly by climatic trial and by experimental work, including the application of the vacuu[m] stability method throughout a range of temperatures. It is no[t,] however, possible to pursue this part of the subject further tha[n] the example already given.

Although the isomerides of trinitrotoluene cause a somewh[at] greater gas evolution with pure ammonium nitrate than th[e] symmetrical compound, the effect of certain impurities in th[e] ammonium nitrate is very much greater. The violence with whi[ch] ...idine reacts with the more highly nitrated aromatic compoun[ds] ... nitro groups ortho to one another h...

been the subject of investigation in the Research Department, and it was accordingly of interest when ammonium nitrate containing pyridine was shown to give rise to tumultuous evolution of gas, even in the cold, with the isomerides of trinitrotoluene, but not with the symmetrical compound. The effect of this interaction can be strikingly shown by the frothing over which occurs when amatol 40/60 containing a small quantity of pyridine or ammonium thiocyanate, for this has a similar effect, is melted in a narrow-necked vessel.

Insensitiveness to Impact.—When this characteristic of the amatols is determined by the method described above, it is found that they are insensitive substances, and they are also found to be insensitive to friction. The influence of heat on the amatols has been investigated as to its effect on their sensitiveness, comparison being made with picric acid, and taken as 100 at 15°.

TABLE IX.

Figures of Insensitiveness of Amatols.

	At 15°.	At 50°.	At 80°.
Amatol 80/20	111—120	108	120
Amatol 40/60	111	—	107
Picric acid	100	—	75

The amatols are thus by themselves fairly insensitive mixtures, and heating does not raise their sensitiveness, but this may be appreciably increased by the presence of gritty matter and of certain salts.

Rate of Detonation.—This was determined by the Mettegang and Dautriche methods already mentioned. The values for the amatols and trinitrotoluene were found to be as follows.

TABLE X.

Rates of Detonation of Amatols.

	Metres per second.	
Trinitrotoluene (cast) at density 1·57	6950	in steel tube of 0·1 in. thickness of wall.
Amatol 40/60 (cast) at density 1·55	6470	
Amatol 80/20 at density 1·3	4620	
" " 1·5	5080	
" " 1·5	5200	in tube 0·24 in. thick.

Two points of interest appear from this table: addition of ammonium nitrate up to 40 per cent. has comparatively little effect in reducing the rate of detonation much below that of trinitrotoluene, and the rate of detonation of 80/20 amatol is still of the high order of 5000 metres per second, and is little raised

beyond this value when the thickness of the steel wall of the container is increased.

Pressure developed.—In the mixtures of trinitrotoluene with ammonium nitrate, the inorganic salt has been sometimes described as a diluent of the high explosive. So far as the explosive properties of the mixtures are concerned, this is an erroneous view. Thus it has been shown that the total heat energy of the fully compensated 80/20 mixture, as determined experimentally, is the same as the value calculated on the assumption of chemical interaction between the ingredients. Again, the substitution of 40 per cent. of ammonium nitrate reduces the rate of detonation of trinitrotoluene only to a slight extent, and even when 80 per cent. of the salt is present, the rate of detonation is still of a high order. Ammonium nitrate, however, is much more than a convenient source of oxygen, for it can be shown by the quantitative method of the pressure-bar that it can by itself break up explosively with a certain degree of violence.

The following table gives the pressures developed under the same conditions of confinement when ammonium nitrate alone and incorporated with 5, 10, 15, and 20 per cent. of trinitrotoluene, all at density of loading of 1·3, are detonated by the help of the same initiating system. Amatol 40/60 and trinitrotoluene, both in the cast condition, are included for comparison.

TABLE XI.

Pressures Developed by Ammonium Nitrate and Amatols.

Ammonium Nitrate.	Trinitrotoluene.	Tons per sq. inch in $0·5 \times 10^{-5}$ sec.
100	0	12·5
99·5	0·5	15·2
99	1	18·3
98	2	20·0
95	5	25·2
90	10	30·5
80	20	38·1
40 (at density 1·55)	60	53·9
0 (at density 1·55)	100	55·0

A correction of 3 tons has to be deducted for the effect of this initiating impulse, but after this allowance has been made, it will be seen that ammonium nitrate has developed a considerable proportion of the pressure associated with the performance of 80/20 amatol, although it will be observed that small proportions of trinitrotoluene have the effect of activating the ammonium nitrate to a much greater extent than the quantity added would apparently warrant, an indication in itself of the explosive nature

of the ammonium nitrate. It is thus clear that in amatol the ammonium nitrate contributes, not only oxygen to supply the deficit of trinitrotoluene in this respect, but it also behaves in the mixture as the explosive which it is.

Amatol 40/60, which was always used in the cast form, and so had usually a higher density, gives higher pressures than amatol 80/20. Its violence, approaching that of trinitrotoluene as thus measured, is in line with its rate of detonation, which, as has been shown, is little below that of trinitrotoluene, in spite of the 40 per cent. of ammonium nitrate present in the mixture.

Having now described some of the properties and constants of the amatols, it is not necessary to go further into the performance of this explosive, of which the type 80/20 was used in such enormous quantities during the war. It is sufficient to say that it met the demands of the fighting forces and received their commendation.

Before concluding this address, I should like to take the opportunity of referring to the work of my colleagues, past and present, on the scientific staff of the Research Department, Woolwich.

They have devoted themselves with enthusiasm to the study of the chemical and physical problems involved, and to the pursuit of methods of obtaining quantitative knowledge where only qualitative information existed before, and their results have had the three-fold value of advancing scientific knowledge generally, of making it capable of application to matters of national importance, and of indicating directions for further work.

I.—*Preparation of Chloropicrin from Picric Acid* and Trinitrotoluenes.*

By KENNEDY JOSEPH PREVITÉ ORTON and PHYLLIS VIOLET MCKIE.

CHLOROPICRIN was first prepared by Shenstone (*Annalen*, 1847, **66**, 241) from picric acid by the action of bleaching powder, chlorine, potassium chlorate and hydrochloric acid, or aqua regia. Hofmann (*ibid.*, 1866, **139**, 111) described in some detail the procedure when bleaching powder is used. He obtained a yield of 114 per cent., that is, 53 per cent. of the maximum (215 per cent.) if all the nitro-groups of the picric acid appear in the chloropicrin:

$$C_6H_2(NO_2)_3\cdot OH \longrightarrow 3CCl_3\cdot NO_2.$$

* Orton and Pope: English Patent, No. 142878 (1918).

Hofmann's yield is undoubtedly low; there is no difficulty in obtaining a yield of 150—160 per cent., a figure which is somewhat above the yield of 143·5 per cent., which corresponds with the appearance of two nitro-groups as chloropicrin:

$$C_6H_2(NO_2)_3 \cdot OH \longrightarrow 2CCl_3 \cdot NO_2.*$$

A consistently better yield, reaching 200 per cent., can be obtained by passing chlorine into a cooled suspension of picric acid (sodium picrate) in aqueous sodium carbonate. The products are chloropicrin and some nitric acid, together with chloride and some hypochlorite, and chlorate which has arisen from transformation of hypochlorite. No other compounds are present in appreciable quantity. From determinations of the hypochlorite, chlorate, and chloride in the aqueous product, it is found that the proportion of the last accords well with the opinion that chloropicrin is formed in a reaction between hypochlorite (hypochlorous acid) and picric acid, thus:

$$C_6H_2(NO_2)_3 \cdot OH + 11HClO = 3CCl_3 \cdot NO_2 + 2HCl + 3CO_2 + 6H_2O,$$

that is,

$$C_6H_2(NO_2)_3 \cdot OH + 11Cl_2 + 5H_2O = 3CCl_3 \cdot NO_2 + 13HCl + 3CO_2, \quad (A)$$

when the maximum yield would be 215 per cent.; or,

$$C_6H_2(NO_2)_3 \cdot OH + 12Cl_2 + 8H_2O = 2CCl_3 \cdot NO_2 + 18HCl + 4CO_2 + HNO_3, \quad (B)$$

when the maximum yield would be 143·5 per cent.

When the yield of chloropicrin is low, however, other substances appear among the products.

The quantity of nitric acid in the product (determined by boiling with excess of ferrous chloride and measuring the nitric oxide evolved) is a measure of the extent to which the reaction has followed a course other than that represented by equation *A*. Nearly the whole amount of nitro-group of the picric acid—up to 96—97 per cent.—is accounted for by the chloropicrin and the nitric acid; probably most of the deficiency is due to want of precision in measurement and to the loss of chloropicrin by evaporation during the preparation.

Effect of Degree of Alkalinity on the Reaction.—According to equation *A*, 23 equivalents of alkali are required by the left-hand side of the equation. The right-hand side, however, only needs 19 equivalents. Hence during the reaction the alkalinity would increase if 23 equivalents were used initially. Moreover,

* Since the work described in this paper was completed, Gardner and Fox (T., 1919, 115, 1188) have recorded that the yield by the Shenstone-Hofmann method can be raised to 180—190 per cent. when the proportion of the reagents and the quality of the bleaching powder are right.

6 of these 19 equivalents are required by carbon dioxide, regenerating carbonate, which is again available for reaction with chlorine. Hence the minimum proportion of alkali for the reaction represented by equation *A* is 13 equivalents. In equation *B*, 25 equivalents of alkali are required on the left-hand side and 27 on the right-hand side; of these, again, 8 are in the form of carbonate and therefore available; hence the minimum number is 19.

In practice, since under the best conditions, nitric acid is always formed, and therefore the reaction in part follows equation *B*, it is best to use 15—17 equivalents of alkali.

In strongly alkaline media, such as sodium hydroxide in place of *sodium carbonate, the yield is greatly diminished.* When the sodium hydroxide is concentrated the reaction is very slow, for the solubility of the picrate is depressed, and, moreover, only hypochlorite, and not hypochlorous acid, is present at least in the initial stages. At the same time a red solid appears as a product. If the concentration of the sodium hydroxide is kept below $0{\cdot}1N$ and the hydroxide (13 equivalents in all) added gradually during the reaction, the yield of chloropicrin is as good as when sodium carbonate is used.

When bleaching powder is used, calcium hydroxide would be formed, if the reaction follows that course (equation *A*) in which the maximum yield is obtained, thus:

$$2C_6H_2(NO_2)_3{\cdot}OH + 11Ca(OCl)_2 = 6CCl_3{\cdot}NO_2 + 6CaCO_3 + 2CaCl_2 + 3Ca(OH)_2.$$

(Using bleaching powder containing 30 per cent. of "active chlorine," 1 part of picric acid would require 3·4 parts of bleaching powder.) Owing to the low solubility of calcium hydroxide, the aqueous medium, in which probably the reaction only takes place, *will not have an alkalinity above 0·04—0·02N*, which would not be an unfavourable degree of alkalinity.

TABLE I.

Alkali.	Yield of chloropicrin. Per cent.
NaOH, 23 equivalents. Concentration: *N*.	110
Na_2CO_3, 9 equivalents; NaOH, 8 equivalents. ...	162
Na_2CO_3, 17 equivalents	194
Soda ash (Na_2CO_3, 90 per cent.; NaOH, 5 per cent.)	194
Na_2CO_3, 12 equivalents; $NaHCO_3$, 5 equivalents...	196

The temperature was in all experiments 2—5°.

The Effect of Temperature.—A low temperature is favourable to the yield of chloropicrin, that is, to the reaction represented by

equation *A*. In table II, 17 equivalents of sodium carbonate were used throughout.

TABLE II.

Temperature.	Yield.
16—17°	168 per cent.
13—14·5°	173
10°	182
2—5°	192—194
0°	198—199

Only a small amount of heat is set free in the reaction when sodium carbonate is used.

Effect of the Presence of Sodium Chloride.—The presence of sodium chloride is deleterious to the reaction, in which chloropicrin is formed thus: in 18 per cent. aqueous sodium chloride the yield was 149 per cent., and in 30 per cent. sodium chloride 92 per cent. The "red solid" is formed in considerable proportion, especially in the more concentrated salt solution. Owing to the depression of solubility in water of chlorine by sodium chloride, the gas is absorbed poorly. Further, the high concentration of chloridion keeps the concentration of free hypochlorous low (Jakowkin, *Zeitsch. physikal. Chem.*, 1899, **29**, 613), and the solubility of the sodium picrate is depressed by the sodium chloride; hence the reaction will be retarded. Again, the concentration of chlorine will be greater, and any reaction with picric acid not leading to chloropicrin therefore favoured. Use of the filtrate (which contains about 8 per cent. of sodium chloride) from one operation is therefore inadvisable; a second re-use causes a serious diminution of yield.

It is not improbable that this effect of chloride accounts for the great influence of "quality" of the bleaching powder on the yield of chloropicrin when this agent is used.

EXPERIMENTAL.

Picric acid is dissolved in a hot solution of 4 parts of sodium carbonate (17 equivalents) in 50 parts of water. On rapidly cooling, sodium picrate separates in small crystals. Large crystals should be avoided. The thin paste is cooled to below 5°, and stirred slowly while a current of washed chlorine is introduced. The treatment with chlorine should either be intermittent or fairly slow. Too rapid a current of chlorine not only leads to loss of gas, but also to the production of chlorate. The speed of the reaction is mainly determined by the size of the crystals of the sodium picrate. The sodium picrate gradually dissolves, and ultimately a colourless oil and a colourless solution are obtained. When industrial chlorine

has been used the oil is yellow. The oil can easily be directly separated from the aqueous layer or distilled in a current of steam. It amounts to 1·17 parts by volume, and is approximately pure chloropicrin.

Solubility of Chloropicrin in Water.—At 10° the solubility is about 0·058 gram per 100 c.c. It rises somewhat with the temperature. By vigorous distillation 75 per cent. of the chloropicrin can be recovered from the solution. A smaller proportion can be salted out. The aqueous solution is stable for a long period, and remains neutral after boiling for some time.

Action of Hypochlorite Solution on o- *and* p-*Mononitro- and* 2:4-*Dinitro-phenol.*—2:4-Dinitrophenol behaves much as picric acid. There is a greater development of heat, and ultimately a colourless oil and solution are obtained. The yield of chloropicrin is only 50 per cent. of the maximum.

p-Nitrophenol gives at first a heavy precipitate, which ultimately dissolves, yielding a colourless oil and solution. The yield of chloropicrin is 33—34 per cent. of the maximum. *o*-Nitrophenol gives a deeply coloured precipitate and liquid. The solid resists treatment with hypochlorite. The yield of chloropicrin is only 10 per cent. of the maximum.

Action of Hypochlorite on Trinitrotoluene and on Trinitrotoluene Residues.—As these materials are insoluble in alkali, contact is most easily effected by "sludging" with water and bleaching powder. As a result of many trials, the proportion of 1 part of nitro-compound to 15 parts of bleaching powder ("active chlorine," 29 per cent.) and 25 parts of water were found best. The mixture is gradually heated, and then a current of steam passed through. If the mixing has been thorough, the colour of the paste is completely discharged, save from trinitrotoluene residues.

TABLE III.

Material used.	Yield as a percentage of weight of material used.
T.N.T., Grade I.	82
T.N.T., Grade III.	84
T.N.T., "residues"	70
Dinitrotoluene	4
s-Trinitrobenzene	53

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[*Received, November 22nd*, 1920.]

II.—*The Decomposition of Tartaric Acid by Heat.*

By Frederick Daniel Chattaway and Francis Earl Ray.

Although the decomposition which tartaric acid undergoes when heated has been studied many times during the past hundred years there is no general agreement as to the substances produced or as to their relative amounts, nor has the course of the decomposition been made clear.

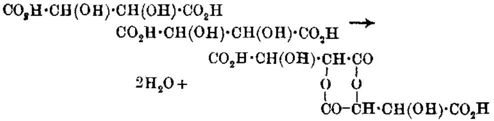
Since many of the products described by previous observers are obviously the result of secondary reactions, the decomposition has been carried out at the lowest possible temperature and under diminished pressure. As under these conditions the primary products are removed immediately they are formed, any side-reactions might be expected to be avoided or reduced to a minimum.

When heated in this way no substances of complicated structure are formed, but the tartaric acid decomposes in two stages; in the first, water alone is liberated; in the second, carbon monoxide and carbon dioxide are produced, together with formic, acetic, and pyruvic acids.

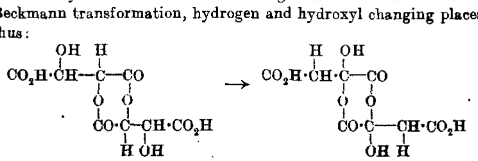
The reactions which occur during the heating may be explained as follows:

The tartaric acid at first loses one molecule of water, and there is produced a solid, colourless substance of the nature of a lactide having half the acidity of the parent acid and reconvertible into it by hydrolysis

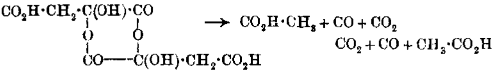
This stage may be formulated thus:



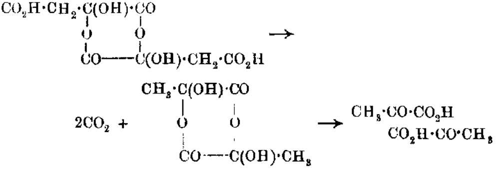
This loss of water must be followed at a somewhat higher temperature by an intramolecular rearrangement of the nature of the Beckmann transformation, hydrogen and hydroxyl changing places, thus:



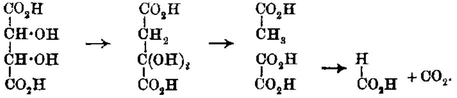
The compound momentarily formed in this manner then breaks down in two ways, producing in one decomposition carbon monoxide, carbon dioxide, and acetic acid, thus:



and in the other decomposition carbon dioxide and pyruvic acid, a *transference of hydroxyl again taking place, thus:*



The formic acid which is produced in small amount in the decomposition is probably formed by an intramolecular rearrangement of the undehydrated acid, followed by a rupture of the molecule similar to that which occurs when a tartrate is fused with sodium hydroxide, the oxalic acid which is one of the primary products of the decomposition subsequently breaking down into carbon dioxide and formic acid.



EXPERIMENTAL.

The heating was carried out in a bath of fusible metal, the bulb of the flask being completely immersed. Reduction of pressure was effected by a water-pump or by a Sprengel pump when the gases were to be examined. Heating was not begun until the pressure had been reduced as far as possible. During the heating a pressure of 10—20 mm was maintained, the pressure varying somewhat with the stage of the decomposition and the rapidity of the accompanying evolution of gas.

The liquid products were condensed in one or more strongly cooled

receivers, whilst the escaping gases, after having been passed through cotton-wool, were collected over mercury.

Tartaric acid, when heated in this way, melts when the temperature of the bath reaches about 150°, and appears to boil vigorously, a clear, colourless liquid condensing in the receivers. If the pressure is kept at 10—15 mm. and the temperature of the bath not allowed to rise above 165°, the distillate is neutral, but it becomes slightly acid if this temperature is exceeded. As the decomposition proceeds, the temperature of the bath being raised a few degrees above 165°, the contents of the flask gradually become more visoid, a slight evolution of gas occurs, and care is needed to prevent the mass distended by this gas and by water-vapour from frothing over.

After some time the frothing ceases, liquid no longer condenses, and action at this temperature appears to come to an end. The contents of the flask, if cooled at this stage, have a white, spongy appearance somewhat resembling dried bread.

When the temperature of the bath is further raised to about 180° action recommences, the mass darkens slightly, gas is very freely evolved, and a clear, yellow liquid of a pungent odour distils over. This decomposition continues until the whole mass has disappeared, a very slight carbonaceous residue only being left behind in the flask. When a low pressure is maintained and the heating is slowly and carefully conducted, this small amount of residue is unweighable and negligible.

The liquid obtained in the first stage of the decomposition is water, 1 gram-molecule approximately beiug given off by each gram-molecule of tartaric acid.

The colourless, spongy solid then remaining is undoubtedly a compound of the nature of a lactide. It is brittle, absorbs moisture from the air, and therefore becomes sticky on exposure. It does not dissolve appreciably in benzene, chloroform, or ether.

It dissolves very sparingly in cold water, more freely in hot. When *quickly dissolved in cold water it is neutralised by little more* than half the amount of alkali required to neutralise the parent acid. Such a neutralised solution becomes again acid on keeping or heating, until finally the amonnt of alkali required for neutralisation equals that which would have been required to neutralise the tartaric acid from which it was derived. On thus neutralising a large amount with potassium hydroxide and crystallising the salt in eight successive crops, each proved to be ordinary neutral potassium tartrate. On boiling it with ethyl alcohol and distilling under reduced pressure ethyl tartrate was obtained.

The gas obtained in the second stage of the decomposition con-

sisted of carbon monoxide and carbon dioxide roughly in the proportion of one volume of monoxide to two volumes of dioxide.

If the first stage of the heating is not carried out very slowly and the temperature of the bath is allowed to rise rapidly to effect complete decomposition more quickly, the percentage of carbon dioxide in the evolved gas is considerably increased owing to the greater amount of tartaric acid decomposing without the initial formation of the lactide.

The liquid distilling in the second stage of the decomposition is a mixture of formic, acetic, and pyruvic acids, no other substances being produced.

By fractionation under diminished pressure the distillate was resolved into its three constituents, and each was separately purified and identified. The amount of each acid yielded by a known weight of tartaric acid was estimated, the formic acid by Franzen and Greve's method (*J. pr. Chem.*, 1909, [ii], **80**, 383), the acetic acid by titration, and the pyruvic acid by conversion into its *p*-bromophenylhydrazone. The average of several concordant estimations gave the following as the products obtainable by the distillation of 1 gram-molecule of tartaric acid (150 grams) under diminished pressure and at a temperature not much exceeding 180°: water, 18·8; formic acid, 2·4; acetic acid, 49; pyruvic acid, 14·1; *carbon monoxide*, 21·3; *carbon dioxide*, 43 *grams*, a *total* less by 1·4 grams than the weight of acid used.

The substances termed by Fremy (*Annalen*, 1839, **29**, 142) tartralic and tartrelic acids represent stages in the formation of the acid lactide, which, together with water, is the sole product of the first stage of the decomposition.

The formation of tarry matters and the subsequent charring which occur when tartaric acid is heated under the ordinary pressure are due to the decomposition of the pyruvic acid first formed, and in no respect differ from the changes which take place when this acid is similarly heated.

THE QUEEN'S COLLEGE, OXFORD. [*Received, November 26th*, 1920.]

III.—*Trithiocarbonates and Perthiocarbonates.**

By Ernest Wickham Yeoman.

The fact that carbon disulphide reacts with soluble sulphides was first observed in 1824 by Zeise, and the products were more fully investigated by Berzelius in 1826 (*Ann. Phys. Chem.*, 1826, [ii], **6**, 450), who showed that the salts produced are the sulphur analogues of the carbonates, and may be regarded as formed by direct combination of carbon disulphide and sulphide. Berzelius prepared soluble and insoluble trithiocarbonates of most of the then known metals, but pointed out, that owing to their instability and ready loss of carbon disulphide, it was very difficult to obtain them in a pure condition. Since that date numerous publications refer to the formation and preparation of trithiocarbonates,† but except in the case of a number of double salts of calcium trithiocarbonate and calcium hydroxide, scarcely any of these appear to have been obtained in a pure condition. In addition, organic derivatives of orthothiocarbonic acid, $C(SH)_4$, have been prepared, such as ethyl orthothiocarbonate (Claesson, *J. pr. Chem.*, 1877, [ii], **15**, 212), but as in the case of the corresponding orthocarbonic acid no inorganic salts have been obtained.

It was generally supposed that the absorption of carbon disulphide from crude coal gas, when this is purified by means of lime, was due to its absorption by calcium sulphides with the formation of calcium trithiocarbonate. Colman (Thorpe's "Dictionary of Applied Chemistry," 2nd edition, article "Coal-gas"), as the result of an investigation of the absorption of carbon disulphide by "sulphided lime," suggested that the active compound was calcium disulphide, which readily combines with carbon disulphide at the ordinary temperature, forming, not the trithiocarbonate, but a new salt, the perthiocarbonate, $CaCS_4$, thus, $CaS_2 + CS_2 = CaCS_4$. This at once accouuts for the known necessity for the presence of some oxygen for absorption to take place, oxygen in limited quantity being required to bring about the formation of the disulphide from the hydrosulphide first produced, $2Ca(SH)_2 + O_2 = 2CaS_2 + 2H_2O$.

Colman drew this conclusion, since he found that the soluble monosulphides or hydrosulphides, free from any polysulphide, had

* Abstract of Thesis approved for M.Sc. Degree (London).

† These salts are commonly termed "thiocarbonates," but the same term is sometimes used for the derivatives of monothiocarbonic acid, **HS·CO·OH** or **HO·CS·OH**. To avoid confusion, the term "trithiocarbonate" is used throughout this communication for the derivatives of the acid **HS·CS·SH**.

little, if any, action on carbon disulphide at the ordinary temperature, but that if sufficient sulphur were added to convert them into the disulphides, the reaction with carbon disulphide took place rapidly, with considerable evolution of heat and the formation of a completely soluble product. If, however, more sulphur were added than was required to produce the disulphide of the metal, the combination with carbon disulphide took place equally rapidly, but the extra sulphur added over and above that required to form the disulphide was then precipitated as elementary sulphur. It was also found that solutions of the normal trithiocarbonates readily dissolved sulphur, and that the amount of sulphur taken up by any of these trithiocarbonate solutions was limited to one atom for each molecule of trithiocarbonate present. All these results pointed to the existence of a series of thiocarbonates containing one more atom of sulphur than the salts usually termed the trithiocarbonates; these may be regarded as salts of the acid H_2CS_4, which may be called perthiocarbonic acid. The detailed results of this investigation were not published, as it was found that almost similar observations had been published by Gélis (*Compt. rend.*, 1875, **81**, 282).*

Since that date K. A. Hofmann (*Zeitsch. anorg. Chem.*, 1897, **14**, 263; *Ber.*, 1903, **36**, 1146) has described numerous double thiocarbonates obtained by the action of carbon disulphide on ammoniacal solutions of copper and other metallic salts, and whilst most of these were derivatives of trithiocarbonic acid, H_2CS_3, he also obtained substances which were derivatives of perthiocarbonic acid, H_2CS_4, one of these, the copper salt, having been obtained as bronze crystals, $CuCS_4$, and analysed, but no soluble perthiocarbonate appears yet to have been isolated in a pure condition; the various soluble trithiocarbonates also appear for the most part only to have been obtained in an impure state, and probably have rarely been free from some admixed perthiocarbonate and thiosulphate.

Experimental.

As is well known, the soluble sulphides all undergo hydrolysis in aqueous solution to a considerable extent, and both polysulphides and thiosulphates are formed in the presence of even small amounts of oxygen (Divers, T., 1884, **45**, 696; Bloxam, T., 1900, **77**, 750).

Rule and Thomas (T., 1911, **99**, 558) have shown that pure hydrosulphides of the alkali metals free from thiosulphate may be

* Dammer ("Handbuch der anorganischen Chemie," 1894, Band 2, Theil 1, p. 412) and Beilstein ("Handbuch der organischen Chemie," 1893, Band 1, p. 887) incorrectly refer to these compounds as derivatives of orthothiocarbonic acid, $C(SH)_4$.

obtained by the action of hydrogen sulphide on an alcoholic solution of the ethoxide, and that on addition of sulphur to the solution, pure polysulphides of the metals are obtained. The various sulphides and polysulphides of sodium and potassium required for the preparation of the alkali salts described below have all been obtained in this manner. Air and moisture have been excluded so far as practicable by carrying out all the operations in a current of dry hydrogen.

Methods of Analysis.

Carbon and water were estimated by combustion of the salt mixed with lead chromate. Calcium was estimated as oxalate, the other metals as sulphates. The total sulphur was estimated either by the Carius method or by combustion with lime. Oxidation of the sulphur by bromine or other agents gives low results. To determine whether the compounds formed were pure, other evidence is required besides that of the elementary analysis. For this purpose the quantity of sulphur (*a*) present as thiosulphate, (*b*) evolved on acidification as hydrogen sulphide, (*c*) present as "polysulphide" sulphur, was determined, in addition to the total sulphur. A solution of cadmium chloride was added to a solution of the salt, and the precipitate filtered, etc.; thiosulphate (*a*) was estimated in the solution, and the sulphur evolved on acidification as hydrogen sulphide (*b*) in the precipitate by means of $N/10$-iodine. "Polysulphide" sulphur was estimated by addition of cadmium chloride to another portion of the dissolved salt and determining the excess of sulphur over that present as cadmium sulphide by filtering, washing, and dissolving the precipitate in hydrochloric acid; the "polysulphide" sulphur can then be filtered, etc., and weighed. Alternatively, the precipitate can be dried, extracted with hot benzene, the benzene evaporated, and the residual sulphur weighed.

Sodium Trithiocarbonate.

Two grams of sodium were dissolved in 60 c.c. of absolute alcohol in a flask fitted with a reflux condenser; the air in the flask was displaced with dry hydrogen, and the solution saturated with dry hydrogen sulphide. To the alcoholic solution of sodium hydrosulphide thus obtained, a slight excess of freshly distilled carbon disulphide was added; hydrogen sulphide was immediately evolved, and the colour of the solution became dark red. The solution was warmed to 60°, dry ether added until a faint turbidity appeared, and the flask allowed to cool slowly in a current of hydrogen. The pinkish-yellow, crystalline precipitate was filtered in an atmosphere

of hydrogen, washed with dry ether, and dried in a brisk current of hydrogen at 60° * (Found, C = 7·1; H_2O = 10·4; Na = 26·8; total S = 56·2; S evolved as H_2S = 17·7.† Na_2CS_3,H_2O requires C = 6·97; H_2O = 10·43; Na = 26·72; total S = 55·88; S evolved as H_2S = 18·63 per cent.).

Sodium trithiocarbonate forms very deliquescent needles, which have a pinkish-yellow colour, and give a distinctly red aqueous solution. This colour, especially in dilute solution, seems to be characteristic of all the soluble, true trithiocarbonates, and is markedly different from the distinctive yellow colour of the solutions of the perthiocarbonates. The salt is very soluble in water, and dissolves in alcohol much more readily than the potassium salt, although much less readily than sodium perthiocarbonate. It is insoluble in ether or benzene, both of which liquids precipitate it from alcoholic solution.

It is stable in dry air free from carbon dioxide, but if moisture is present it quickly oxidises and decomposes, losing carbon disulphide. The crystals first deliquesce, then lose their colour, and become solid owing to the formation of sodium thiosulphate and hydroxide, the latter being converted into carbonate in the presence of carbon dioxide. The course of the change is probably:

$$Na_2CS_3 = Na_2S + CS_2;\ Na_2S + H_2O = NaSH + NaOH.$$
$$2NaSH + O = Na_2S_2 + H_2O;\ Na_2S_2 + 3O = Na_2S_3O_3.$$

This receives confirmation from the fact that such a decomposed product contains thiosulphate and has an alkaline reaction, and that in the case of the perthiocarbonates nearly pure thiosulphate results. Unless the carbon dioxide of the air has access, no carbonate is formed.

On strongly heating, the salt decomposes into sodium sulphide and carbon disulphide. If water is absent, the salt is stable when heated in a stream of hydrogen to 60°, but at about 75° carbon disulphide begins to escape, the loss, however, not being very great even at 100°. A current of dry air, free from carbon dioxide, does not cause more decomposition of the dry salt than hydrogen.

An aqueous solution remains stable if oxygen and carbon dioxide are rigidly excluded, but if oxygen is present, loss of carbon disulphide ensues with subsequent hydrolysis and oxidation of the sulphides, producing thiosulphate and polysulphide; the latter then loses sulphur to any unaltered trithiocarbonate, forming perthiocarbonate, which in its turn loses carbon disulphide and by oxida-

* A little xanthate is formed but remains in the solution (compare Holmberg, *J. pr. Chem.*, 1906, [ii], **73**, 239).

† "Polysulphide" sulphur and thiosulphate were present in traces only.

tion is transformed to thiosulphate; the colour of the solution, at first red, becomes yellow and finally vanishes.

Berzelius (*loc. cit.*) gave the following equation for the reaction between water and trithiocarbonates:

$$Na_2CS_3 + 3H_2O = Na_2CO_3 + 3H_2S.$$

It will be shown later that this equation represents the reaction only under certain conditions. Sodium trithiocarbonate, when distilled with air-free water, excluding air and carbon dioxide, gives off hydrogen sulphide and loses all its carbon disulphide, which can be recovered as such in the distillate, and the residue contains sodium sulphide and its hydrolytic products, but no carbonate and only traces of thiosulphate, the latter being due to the presence of a small quantity of air. Tarugi (*Gazzetta*, 1909, **39**, i, 405) also found this to be the case. If a stream of air free from carbon dioxide is drawn through a boiling solution of the trithiocarbonate, only a portion of the carbon disulphide can be recovered; part of it becomes converted to the carbonate, and thiosulphate also remains in the solution. It was found on experiment that varying amounts of the carbon disulphide up to 25 per cent. were thus converted, only partial agreement being obtained with Tarugi (*loc. cit.*), who gives an equation demanding a 50 per cent. conversion:

$$2Na_2CS_3 + 2H_2O + 4O = Na_2S_2O_3 + CS_2 + Na_2CO_3 + 2H_2S.$$

If an air-free solution of the salt is heated in a sealed tube at 100° carbonate is also formed, and on opening the tube much hydrogen sulphide, formed on hydrolysis, escapes. The reactions are as follows:

$$Na_2CS_3 = Na_2S + CS_2;\ Na_2S + 2H_2O = 2NaOH + 2H_2S;$$
$$6NaOH + 3CS_2 = Na_2CO_3 + 2Na_2CS_3 + 3H_2O.$$

The trithiocarbonate formed again decomposes, and the reaction, after prolonged heating, reduces to the one represented by the equation given by Berzelius. Experiment showed that the reaction is never quite complete, the amount of carbonate tending, however, to approach the theoretical amount after a long time. If air is present thiosulphate and polysulphide are formed as well. It should be noted that Chancel and Parmentier (*Compt. rend.*, 1884, **99**, 892) found that on heating carbon disulphide with baryta water more barium carbonate is formed than corresponds with the equation:

$$3CS_2 + 3Ba(OH)_2 = BaCO_3 + 2BaCS_3 + 3H_2O,$$

and that the reaction should be represented by

$$CS_2 + 2Ba(OH)_2 = BaCO_3 + Ba(SH)_2 + H_2O;$$

this is in accord with the above explanation, but the barium hydro-

sulphide is not hydrolysed to such an extent as in the case of the sodium salt.

Carbon dioxide decomposes both the salt and its solution, forming the carbonate and carbon disulphide; it is this reaction that is responsible for the carbonate found by many investigators. Sulphur dioxide converts the salt into the sulphite with loss of carbon disulphide.

A solution of the salt dissolves a constant weight of sulphur, namely, one atom of sulphur to one molecule of trithiocarbonate, thus confirming the observations of Gélis and Colman. If the salt is impure, then the amount of sulphur taken up varies according to the amount of polysulphide that has been formed. This, in conjunction with the results of thermochemical experiments to be described later, confirms the view of Gélis and Colman that a new compound had been formed, differing from the trithiocarbonates in containing an additional atom of sulphur.

Sodium Perthiocarbonate.

Sodium (2·3 grams) was dissolved in 40 c.c. of absolute alcohol in the same manner and with the same precautions that were taken in the preparation of the trithiocarbonate. To this solution a solution of 2·3 grams of sodium in 40 c.c. of alcohol was added, thus forming an alcoholic solution of sodium sulphide, which was converted into the disulphide by the addition of 3·2 grams of sulphur. A slight excess of carbon disulphide was added, the colour of the solution changing from yellow to red. On addition of ether to this perthiocarbonate solution a reddish-yellow oil was precipitated, which slowly solidified to a microcrystalline mass of brownish-yellow needles. On keeping, the filtrate deposited a further amount in nodular aggregates of prismatic, doubly refracting needles. The crystalline mass was collected, washed with ether in an atmosphere of hydrogen, and finally dried at 60° in a stream of the same gas.

Alternatively the sodium disulphide required may be prepared by the direct addition of sulphur to the sodium hydrosulphide without addition of a second molecule of sodium ethoxide, the disulphide being then formed with the evolution of hydrogen sulphide (Rule and Thomas, *loc. cit.*). Working in this manner, thiosulphate is less likely to be present in the perthiocarbonate produced (Found, C=5·2; H_2O=22·2; Na=19·6; total S=53·8; "polysulphide," S=13·7; S evolved as H_2S=13·7.* $Na_2CS_4,3H_2O$ requires C=4·99; H_2O=22·50; Na=19·14; total S=53·37; "polysulphide," S=13·34; S evolved as H_2S=13·34 per cent. $Na_2CS_3,5H_2O$

* Thiosulphate present as a trace only.

requires C=4·92; H_2O=36·86; Na=18·83; total S=39·39; S evolved as H_2S=13·13 per cent.).

The salt is very deliquescent, dissolves readily in water, forming a distinct yellow solution (compare trithiocarbonates), and is soluble in alcohol, being precipitated therefrom by ether or benzene.

In dry air, free from carbon dioxide, the salt is stable, but in moist air it quickly decomposes, losing carbon disulphide, the residue being oxidised to almost pure thiosulphate (Found, Na= 19·3; S=25·4. $Na_2S_2O_3,5H_2O$ requires Na=18·55; S=25·80 per cent.), the reactions on oxidation being:

$$Na_2CS_4 = Na_2S_2 + CS_2;\ Na_2S_2 + 3O + 5H_2O = Na_2S_2O_3,5H_2O.$$

On heating, the dry salt behaves in a similar manner to the trithiocarbonate, except that the disulphide remains in place of the monosulphide.

In the absence of oxygen the aqueous solution remains stable for a long time; if air is present the solution loses carbon disulphide, and becomes colourless, thiosulphate remaining in the solution.

On heating the air-free aqueous solution in a sealed tube thiosulphate is always formed owing to the reaction between the polysulphide sulphur and the hydroxide produced by hydrolysis. On cooling, some sulphur separates, and on opening the tube much hydrogen sulphide escapes. The reactions are the same as in the case of the trithiocarbonate, except that the polysulphide sulphur always gives rise to thiosulphate. Finally, after prolonged heating, nearly all the perthiocarbonate is converted into the carbonate.

A solution of the salt distilled in the absence of air loses all carbon disulphide, which can be recovered as such in the distillate:

0·3180 CS_2 present as perthiocarbonate gave 0·3160 CS_2 in the distillate=99·5 per cent. Carbonate in residue=nil.

If, however, a current of air free from carbon dioxide is passed through the boiling solution, some carbonate is formed, but not to the extent demanded by the equation given by Tarugi (*loc. cit.*), thus:

0·2820 CS_2 present as the perthiocarbonate yielded 0·0120 CO_2= 0·0208; CS_2=7·4 per cent. conversion.

Many such experiments were carried out, but the 50 per cent. conversion was never attained. In every case, the carbonate formed was precipitated as barium carbonate, collected, washed, and treated ith dilute hydrochloric acid, a little potassium dichromate being and th ed to oxidise any sulphide remaining. The carbon dioxide set after drying, was collected in soda–lime tubes and weighed.

this is in acc on dioxide quickly decomposes the salt with the formation of ate and sulphur, and the evolution of carbon disulphide

and hydrogen sulphide. Sulphur dioxide completely converts it into thiosulphate and sulphur with loss of carbon disulphide:

$$2Na_2CS_4 + 3SO_2 = 2Na_2S_2O_3 + 3S + 2CS_2.$$

According to the statements of Gélis, the salt should not dissolve sulphur; experiment confirmed this.

(1) 0·8400 of the salt was dissolved in air-free water and allowed to remain, with shaking, for a long time with 0·2000 of sulphur; on filtering, washing, etc., sulphur recovered = 0·2000 = 100 per cent.

(2) 0·6530 of the salt and 0·5000 of sulphur; sulphur recovered was 0·4930 = 98·6 per cent.

The additional sulphur atom in the perthiocarbonates is readily removable by reagents which have a direct action on sulphur, such as hydrocyanic acid or sodium cyanide. When excess of the latter reagent is added to the pure yellow solution of the perthiocarbonate the colour soon changes from yellow to the characteristic red of the trithiocarbonates, the additional atom of sulphur being removed and converted by the cyanide into thiocyanate.

Heat Evolved by Combination of Carbon Disulphide with (*a*) Sodium Sulphide, (*b*) Sodium Disulphide.

It has already been stated that when carbon disulphide is dissolved in a solution of sodium polysulphide, the reaction is quicker and more heat is evolved than when the monosulphide is employed. The heats disengaged were determined in an approximate manner by employing a simple calorimeter. The results obtained in this way, whilst not possessing a high degree of accuracy, give good comparative figures.

The reactions to be considered take place too slowly in aqueous solution to permit of any calorimetric determinations, so that absolute alcohol was employed as the solvent. It was found that:

(1) $Na_2S + CS_2 + \text{alcohol} = Na_2CS_3 + \text{alcohol} + 5700$ cals.

(2) $Na_2S_2 + CS_2 + \text{alcohol} = Na_2CS_4 + \text{alcohol} + 8550$ cals.

The reactions:

$$Na_2S + S + \text{alcohol} = Na_2S_2 + X \text{ cals.}$$

$$Na_2CS_3 + S + \text{alcohol} = Na_2CS_4 + Y \text{ cals.}$$

ake place too slowly, and the apparatus at the author's disposal lid not permit of other determinations. It is, however, probable hat the values of X and Y would not differ very much from those ound, using water as the solvent. Sabatier (*Compt. rend.*, 1880, 90, 1557) found that:

$$Na_2 + S + S + aq. = Na_2S_2aq. + 103{,}400 \text{ cals.}$$

$$Na_2 + S + aq. = Na_2Saq. + 102{,}000 \text{ cals. } \therefore$$

therefore:

$$Na_2S + S + aq. = Na_2S_2aq. + 1400 \text{ cals.}$$

Assuming that the same evolution of heat occurs in alcoholic solution, then $Na_2CS_3 + S + \text{alcohol} = Na_2CS_4 + \text{alcohol} + 4290$ cals.

Hence, in the formation of the perthiocarbonate by the addition of sulphur to the trithiocarbonate, the heat evolved is three times that evolved in the formation of the disulphide from the monosulphide. It therefore appears unlikely that mere solution or polysulphide formation has taken place.

Potassium Trithiocarbonate.

Two grams of potassium were dissolved in absolute alcohol and converted into the hydrosulphide with the same precautions as were taken in the preparation of the sodium salt, the temperature of the solution being kept at 45—50° and the proper amount of carbon disulphide added. On allowing the solution to cool slowly, a yellow, crystalline substance separated, which was collected, washed with dry ether, and dried in a brisk current of dry hydrogen at about 45° (Found, C = 6·1; H_2O = 1·0; K = 41·6; total S = 50·9; S evolved as H_2S = 17·0.* K_2CS_3 requires C = 6·44; K = 41·95; total S = 51·61; S evolved as H_2S = 17·20 per cent.).

The salt can thus be considered as anhydrous; further efforts to remove the last traces of water resulted in its decomposition. The salt behaves in a manner entirely analogous to sodium trithiocarbonate, it is less readily soluble in alcohol, but exceptionally deliquescent in moist air; aqueous solutions have the typical red colour, and are capable of dissolving one atom of sulphur for every molecule of the salt.

Potassium Perthiocarbonate.

Two grams of potassium were converted into the polysulphide with the usual precautions; this was brought to a temperature of 40°, and the requisite amount of carbon disulphide added; on cooling slowly a yellow, crystalline substance separated (not an oil, as in the case of the sodium salt), which was collected, washed with dry ether, and dried in hydrogen at 45—50° (Found, C = 5·3; H_2O = 4·7; K = 34·6; total S = 56·2; "polysulphide" S = 14·0; S evolved as H_2S = 14·1.† $K_2CS_4,\frac{1}{2}H_2O$ requires C = 5·28; H_2O = 3·96; K = 34·39; total S = 56·37; "polysulphide" S = 14·09; S evolved as H_2S = 14·09 per cent.).

Attempts to dry the salt further resulted in its decomposition.

* "Polysulphide" and thiosulphate present in traces only.

The salt behaves in a similar way to the corresponding sodium compound; it is more deliquescent, less readily soluble in alcohol, and, like all the perthiocarbonates, will not combine with sulphur.

Calcium Trithiocarbonates.

All attempts to prepare the simple trithiocarbonate gave double compounds of calcium trithiocarbonate and calcium hydroxide of the type previously described by Sestini (*Gazzetta*, 1871, **1**, 473), Walker (*Chem. News*, 1874, **30**, 28), Veley (T., 1885, **47**, 478), and O'Donoghue and Kahan (T., 1906, **89**, 1812). From aqueous solutions the author obtained reddish-yellow needles of the composition $3Ca(OH)_2,CaCS_3,9H_2O$, and from alcoholic solutions similar needles corresponding with the formula $Ca(OH)_2,CaCS_3,2H_2O$. These basic compounds are more stable than the trithiocarbonates of sodium and potassium, probably because they are less hygroscopic; in other respects they behave in a similar manner. It may be pointed out that in the case of these basic salts it is scarcely possible to decide on the evidence of the elementary analysis alone, whether they consist of basic trithiocarbonates or basic perthiocarbonates; to decide this point, the amount of sulphur evolved as hydrogen sulphide or precipitated as sulphur on the addition of acid must be determined, as well as the total sulphur. The colour of the dilute solution and its action on sulphur afford further evidence. The compounds described above evolve one-third of their sulphur as hydrogen sulphide on acidification, give no polysulphide sulphur in dilute solution, have the characteristic colour of the trithiocarbonates, and dissolve sulphur, forming the yellow perthiocarbonate solution.

Calcium Perthiocarbonates.

Pure lime was converted into an aqueous solution of the polysulphide with the usual precautions, the polysulphide then converted to the perthiocarbonate by the passage of a stream of hydrogen saturated with carbon disulphide vapour, and on evaporating the solution in a vacuum dark red needles were deposited (Found, C = 2·2; H_2O = 34·6; Ca = 24·4; total S = 26·4; polysulphide S = 6·7; S evolved as H_2S = 6·6.* $CaCS_4,2Ca(OH)_2,8H_2O$ requires C = 2·54; H_2O = 38·14; Ca = 25·43; total S = 27·12; polysulphide S = 6·78; S evolved as H_2S = 6·78 per cent.).

If alcoholic solutions were employed, addition of ether precipitated oils which took a long time to crystallise; the crystals dis-

* Thiosulphate present as a trace only.

solved in water, forming yellow solutions, which gave the reactions for the perthiocarbonates, but contained large and varying amounts of thiosulphate. On drying in a vacuum or in a current of hydrogen, they decomposed, leaving a residue of hydrated calcium polysulphides.

Barium Trithiocarbonate.

Veley (T., 1886, **49**, 369) states that although barium trithiocarbonate exists as a yellow substance, yet owing to its instability he was unable to analyse it. Holmberg (*loc. cit.*), by the action of barium chloride and formaldehyde on a freshly prepared solution of potassium trithiocarbonate, obtained a yellow, amorphous substance, the analysis of which agreed with the formula $BaCS_3$. In view of these facts Veley's experiments were repeated.

An aqueous solution of barium hydrosulphide was prepared from the hydroxide with the usual precautions, and this converted to the trithiocarbonate by passage of hydrogen saturated with carbon disulphide. Addition of alcohol to this red solution precipitated a yellow substance, which was collected and dried in a current of hydrogen or in a vacuum (Found, C = 4·9; Ba = 55·8; total S = 39·4; S evolved as H_2S = 13·7; polysulphide S = 0·3; S as thiosulphate = 0·4. $BaCS_3$ requires C = 4·90; Ba = 55·95; total S = 39·15; S evolved as H_2S = 13·05 per cent.).

This compound can also be prepared in a slightly different way by suspendiug barium hydroxide free from carbonate in alcohol and removing the air with hydrogeu; on passing a stream of hydrogen saturated with carbon disulphide vapour, the barium hydroxide finally disappears, and a yellow precipitate remains, which is collected and dried in a vacuum (Found, C = 5·2; Ba = 56·0; S = 39·0 * per cent.).

The yellow substance formed in either way is microcrystalline, insoluble in alcohol, and sparingly soluble in water, giving a red solution. Berzelius noted that the dilute solution was red, but thought that the proper colour was yellow. Contrary to the statements of Veley, the salt is comparatively stable, for whereas all the other trithiocarbonates gradually decompose when kept in a stoppered bottle, the barium salt remains unchanged for a very long time, this being probably due to the fact that it is less hygroscopic than the other salts.

A solution of the salt dissolves one atom of sulphur for each molecule of barium trithiocarbonate, the colour changing from red to yellow, for example:

(1) 0·6040 $BaCS_3$ was dissolved in air-free water, the vessel being

* Thiosulphate and polysulphide were present in traces only.

filled to the cork, 0·5500 pure sulphur added, and the vessel allowed to remain with continual agitation for a long time. After filtering, etc., the sulphur remaining was 0·4640. Sulphur dissolved = 0·0860 = 14·2 per cent. of the $BaCS_3$.

(2) $BaCS_3$ taken 1·9360; S dissolved 0·2590 = 13·5. $BaCS_3$ by theory can take up S = 13·04 per cent.

The variation from the theoretical is due to the fact that the salts used were not completely pure; the solution obtained from the latter experiment was mixed with sulphur, and after eight weeks the extra sulphur dissolved was only 0·0020 gram.

Barium trithiocarbonate behaves in a similar manner to the sodium salt on heating both when dry and in aqueous solution, and in its behaviour towards acids, etc.

Barium Perthiocarbonate.

It was found, as stated above, that a solution of barium trithiocarbonate will dissolve one atom of sulphur per molecule, and experiments showed that a solution of barium hydrosulphide with the necessary sulphur to correspond with the formula BaS_2 (this compound has not been isolated) would dissolve carbon disulphide more readily and with greater evolution of heat than if the hydrosulphide were employed. This is in conformity with the results obtained with the other sulphides and polysulphides; it seemed reasonable to conclude, therefore, that the perthiocarbonate existed, at least in solution. All attempts to isolate the solid failed; alcohol precipitated a mixture of sulphur and more or less pure trithiocarbonate; on evaporation of solutions which should contain perthiocarbonate in a vacuum, oxidation always took place with the formation of white crystals (Found, Ba = 51·4; S = 24·5. $Ba_2S_2O_3,H_2O$ requires Ba = 51·39; S = 23·93 per cent.).

Strontium Trithiocarbonate.

Ten grams of strontium hydroxide were suspended in 60 c.c. of 95 per cent. alcohol and converted into the hydrosulphide by passing hydrogen sulphide, the temperature being kept at about 70° and air being excluded as usual. Carbonate, which was always present, was removed by filtration in an atmosphere of hydrogen; a slight excess of carbon disulphide was added to the filtered solution, which was allowed to remain with exclusion of air for thirty minutes at 40°. Addition of ether to this solution precipitated dark red needles which became yellow on drying in a vacuum (Found, C = 4·4; H_2O = 27·0; Sr = 32·6; total S = 36·1; S evolved as H_2S =

12·8.* $SrCS_3,4H_2O$ requires C = 4·48; H_2O = 26·89; Sr = 32·71; total S = 35·92; S evolved as H_2S = 11·97 per cent.).

Strontium trithiocarbonate is much more readily soluble in water than the barium or basic calcium salts.

Strontium Perthiocarbonate.

Ten grams of strontium hydroxide were suspended in alcohol and converted into the hydrosulphide as above. The calculated amount of sulphur was added to form the disulphide, which was then converted into the perthiocarbonate by addition of carbon disulphide. Addition of ether to the alcoholic solution precipitated a red oil, which crystallised after some time, forming yellow crystals, which were collected, washed with ether, and dried in a vacuum (Found, C = 2·7; H_2O = 39·0; Sr = 23·7; total S = 34·5; polysulphide S = 8·4; S evolved as H_2S = 8·4.† $SrCS_3,8H_2O$ requires C = 3·22; H_2O = 38·73; Sr = 23·56; total S = 34·49; polysulphide S = 8·62; S evolved as H_2S = 8·62 per cent.).

The yellow crystals dissolve readily in water, forming a yellow solution which is incapable of dissolving sulphur; they are soluble in alcohol, and precipitated by ether as a red oil which requires some time to crystallise (compare potassium and sodium perthiocarbonates).

Magnesium Tri- and Per-thiocarbonate.

Berzelius (*loc. cit.*) prepared magnesium trithiocarbonate by mixing solutions of barium trithiocarbonate and magnesium sulphate, the barium sulphate being filtered off and the solution evaporated in a vacuum; he obtained the salt in citron-yellow crystals which readily formed basic salts. On repeating these experiments, adding the calculated amount of magnesium sulphate to solutions containing (*a*) barium trithiocarbonate, (*b*) barium trithiocarbonate with the requisite amount of sulphur corresponding with $BaCS_4$, and filtering, solutions were obtained containing magnesium trithio- and perthio-carbonate respectively. The trithiocarbonate solution was red and capable of dissolving one atom of sulphur for each molecule of the trithiocarbonate. The perthiocarbonate was yellow and incapable of dissolving sulphur. On evaporating these solutions in a vacuum, yellow substances were obtained, which were basic, but very impure, containing variable and large amounts of thiosulphate.

If magnesium oxide is suspended in alcohol and hydrogen sulphide saturated with carbon disulphide vapour passed in for a long

* Polysulphide and thiosulphate present in traces only.

† Thiosulphate present as a trace only.

time with exclusion of air, then on filtering and precipitating with ether a crystalline substance is obtained which appears to be the trithiocarbonate. In a similar manner the perthiocarbonate is formed by employing a mixture of magnesia and sulphur.

Ammonium Trithiocarbonate.

Ammonia, dried by passing over quicklime, was dissolved in alcohol forming a 20 per cent. solution, and this solution was saturated with dry hydrogen sulphide; after warming to 35—40° and simultaneously passing hydrogen to exclude air, a slight excess of carbon disulphide was added and then dry ether until a permanent turbidity was produced. On allowing the solution to cool slowly, a red, crystalline substance separated, which was collected in hydrogen, washed with dry ether, and dried as completely as possible at the ordinary temperature in a current of hydrogen (Found, C=7·5; NH_4=25·8 *; total S=65·7; S evolved as H_2S=23·1.† $(NH_4)_2CS_3$ requires C=8·33; NH_4=24·96; total S=66·71; S evolved as H_2S=22·27 per cent.).

The salt is soluble in water, giving the typical red solution of the trithiocarbonate; the aqueous solution dissolves sulphur, one atom for each molecule of the salt; it is more readily soluble in alcohol than the perthiocarbonate, and is precipitated from solution by ether. The salt gradually decomposes at the ordinary temperature, first losing carbon disulphide (the analysis shows that the salt has lost some carbon disulphide), forming ammonium sulphide, which in its turn becomes dissociated into ammonia and hydrogen sulphide; on keeping for some time thiocyanate is also formed.

On heating the freshly prepared dry salt in hydrogen at 100° it completely dissociates, leaving no residue. Aqueous solutions of the salt are very unstable, easily losing carbon disulphide, hydrogen sulphide, and ammonia, in addition to which oxidation takes place as with the other trithiocarbonates. On boiling an aqueous solution in an open vessel this change takes place rapidly, very little thiocyanate and no carbamide being formed.

Ammonium Perthiocarbonate.

A 20 per cent. alcoholic solution of dry ammonia was converted into the hydrosulphide and the exact amount of sulphur added to

* The carbon was estimated by heating with alcoholic ammonia in a sealed tube at 100° and determining the thiocyanate formed. In the NH_4 determination the salt was first heated for a short time with concentrated sulphuric acid, since the ordinary procedure would cause formation of thiocyanate.

† Thiosulphate, polysulphide, and thiocyanate were present in traces only.

convert it into the disulphide, $(NH_4)_2S_2$, all the operations being made in the absence of air. On addition of carbon disulphide the perthiocarbonate was immediately precipitated as a yellow, crystalline solid. The crystals were collected, washed with dry ether with the usual precautions, and the ether was removed as completely as possible in a current of hydrogen at the ordinary temperature (Found, C=6·3; NH_4=18·2; total S=66·0; polysulphide S=17·0; S evolved as H_2S=16·3. $(NH_4)_2CS_4,H_2O$ requires C=6·18; H_2O=9·26; NH_4=18·53; total S=66·03; polysulphide S=16·51; S evolved as H_2S=16·51 per cent.).

On allowing an alcoholic solution of ammonium perthiocarbonate to evaporate slowly at the ordinary temperature, well-defined, transparent crystals of the monosymmetric or asymmetric systems were obtained, some of them being 10 mm. long, 7 mm. wide, and 2 mm. thick (Found, C=7·3; H=4·7; N=15·3; total S=73·0; polysulphide S=18·5; S evolved as H_2S=17·7. $(NH_4)_2CS_4$ requires C=6·81; H=4·57; N=15·88; total S=72·74; polysulphide S=18·18; S evolved as H_2S=18·18 per cent.).

The salt is very readily soluble in water, forming a yellow solution which is incapable of dissolving sulphur, but not very easily so in alcohol, being precipitated therefrom by ether. It behaves in a very similar manner to the trithiocarbonate, losing carbon disulphide, hydrogen sulphide, and ammonia at the ordinary temperature, the residue becoming richer in sulphur. It completely decomposes when heated at 100° in a stream of hydrogen, leaving a residue of sulphur. At the ordinary temperature aqueous solutions are only very slowly converted into the thiocyanate, excess of ammonia hastening the reaction. As with the trithiocarbonate, the conversion to thiocyanate is complete if the salt is heated in a sealed tube with alcoholic ammonia at 100°.

The solutions of both ammonium trithiocarbonate and perthiocarbonate are very unstable, partly because of the well-known change which ammonium trithiocarbonate undergoes, whereby it loses hydrogen sulphide in two stages, passing successively into ammonium dithiocarbamate and ammonium thiocyanate, and partly on account of the ready manner in which it undergoes complete dissociation into ammonia, hydrogen sulphide, and carbon disulphide. This dissociation occurs so readily at the ordinary temperature that even inert gases, such as hydrogen and nitrogen, when passed through solutions of the ammonium thiocarbonates containing less than 0·1 per cent. of carbon disulphide, take up the latter to the extent of 1·1 milligrams per litre (50 grains per 100 cubic

Trithiocarbonic and Perthiocarbonic Acids.

Many investigators have found that solutions of the thiocarbonates on treatment with acid yielded a reddish-yellow oil, which soon decomposed, giving off carbon disulphide and hydrogen sulphide, and was supposed to be trithiocarbonic acid, H_2CS_3. O'Donoghue and Kahan (T., 1906, **89**, 1812) determined the sulphur in the dry oil, and found that it agreed with the formula H_2CS_4, but concluded that the oil was a solution of sulphur in trithiocarbonic acid, basing their conclusions on the results of partial analyses of salts prepared from the acid oil. The author was unable to confirm their results, but found that pure trithiocarbonates yielded no oil on addition of acid at 0°, provided oxygen was completely excluded; if oxygen had access or if sulphur or thiosulphate was added to the solution, then the insoluble oil was slowly formed on addition of acid, the amount varying and depending on the extent to which oxygen had access or to the quantity of thiosulphate or sulphur present. Crude thiocarbonates and pure perthiocarbonates, on treatment with acid, yield an oil immediately at the ordinary temperature. The oils obtained in the several cases were converted into salts, great precautions being taken to exclude oxygen; complete analyses of these partly dried salts showed them all to be perthiocarbonates. The formation of perthiocarbonates will equally take place, whether the oil is H_2CS_4 or H_2CS_3+S, but in conjunction with the above it appears likely that the insoluble red oil is *perthiocarbonic acid*, H_2CS_4, and that *trithiocarbonic acid*, H_2CS_3, exists and is soluble in water, for otherwise addition of acid to a cold solution of a pure trithiocarbonate will cause the separation of the almost insoluble carbon disulphide, which separation has not been observed. When oxygen has free access, perthiocarbonate will be produced, as shown earlier in this paper; and if thiosulphate or sulphur is present, the trithiocarbonate will take up sulphur direct or from the thiosulphuric acid formed on the addition of acid, in both cases forming the perthiocarbonate and thence the perthiocarbonic acid.

Colour and Constitution of the Trithiocarbonates and Perthiocarbonates.

The alkyl derivatives of orthothiocarbonic acid and the numerous derivatives of carbonic acid, in which one or two oxygen atoms are displaced by sulphur, are colourless. A priori, it would be expected that the trithiocarbonates would also be colourless, whereas, in fact, even when quite free from perthiocarbonates they have a deep

yellow colour. Whether this colour would persist if the salts were completely anhydrous could not be determined owing to the loss of carbon disulphide on prolonged drying, but the anhydrous alkyl esters are all strongly coloured yellow liquids or deep yellow, crystalline solids. Chancel (*Jahresber.*, 1851, 513) describes the alkyl potassium and alkyl sodium salts of trithiocarbonic acid as colourless, crystalline solids; Holmberg (*J. pr. Chem.*, 1906, [ii], **73**, 239) describes them as yellow substances. On repeating Chancel's experiments, the author obtained yellow, crystalline substances which were far from pure.

The capacity for the direct combination with sulphur appears to be confined to those derivatives of carbonic acid in which all three oxygen atoms are displaced by sulphur, for example, neither sodium xanthate nor ammonium dithiocarbamate is capable of combining with sulphur. Ethyl trithiocarbonate, $(C_2H_5)_2CS_3$, does not combine with sulphur forming the perthiocarbonate, but dissolves sulphur in amounts varying with the temperature. In fact, it was not found possible to prepare ethyl perthiocarbonate, although, as shown by Berend (*Annalen*, 1865, **128**, 333), the alkyl esters are capable of forming additive compounds with one molecule of bromine, which are well-defined, crystalline substances. In many ways the relation of the trithiocarbonates to the perthiocarbonates is analogous to that of the metallic sulphides to the polysulphides. There are certain differences, however, the heat of formation of the combination of trithiocarbonate with sulphur being three times that of the formation of disulphide from monosulphide, and whereas the trithiocarbonates can only combine with one extra atom of sulphur, the sulphides can combine with as many as five or six.

In conclusion, the author wishes to record his indebtedness to Dr. H. G. Colman, both for valuable advice and for the opportunity of carrying out this work.

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[Received, November 3rd, 1920.]

IV.—*The Bromine Compounds of Phenanthrene. Part I.*

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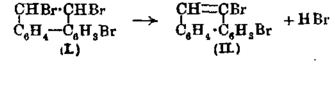
WHEN it is considered that phenanthrene is one of the principal aromatic hydrocarbons derived from coal-tar, it seems strange that up to now almost the only commercial use to which it has been put is the production of lamp black, by its destruction. Several of the alkaloids, notably morphine, *apo*morphine, and thebaine, have the phenanthrene molecule as the chief basis of their structure, and the hydrocarbon should also be a fruitful source of colouring matters. One of the chief reasons why its value has not been more appreciated is undoubtedly the very meagre knowledge which we have of its more common compounds. Its halogen derivatives offer a promising field for inquiry.

The number of possible isomeric bromophenanthrenes is large, although few have been already described, and still fewer thoroughly investigated.

Of the five possible monobromo-derivatives, only 9-bromophenanthrene (m. p. 63°) is known (Hayduck, *Annalen*, 1873, **167**, 181). Of the twenty-five possible dibromo-derivatives only six are known, namely, the 2 : 7 (m. p. 199—200°; Hayduck, *loc. cit.*; Schmidt and Mezger, *Ber.*, 1907, **40**, 4562), the 9 : 10 (m. p. 181—182°; Hayduck, *loc. cit.*; Schmidt and Ladner, *Ber.*, 1904, **37**, 4404), the 3 : 9 (m. p. 146°; Zetter, *Ber.*, 1878, **11**, 170; Schmidt and Ladner, *Ber.*, 1904, **37**, 3571; Sandqvist, *Ber.*, 1920, **53**, [*B*], 168), the 4 : 9 (or 10) (m p. 113°, Werner, *Annalen*, 1902, **321**, 331), the 10 : (1, 4, 5 or 8) (m. p. 123°, Sandqvist, *Ber.*, 1915, **48**, 1146), and a dibromo-derivative melting at 202° (*Annalen*, 1873, **167**, 182). With the exception of two or three imperfectly described ones, nothing is known of the sixty-one possible tribromo-derivatives. In brominating phenanthrene, the 9 : 10-positions are those most readily attacked, and this dibromide is very unstable, decomposing at 100° with the evolution of hydrogen bromide and the formation of the 9-bromo-derivative (Hayduck, *loc. cit.*).

In the course of this work a 2(?)-*bromophenanthrene dibromide* (I) was isolated, which decomposed exactly as in the case of Hayduck's dibromide (*loc. cit.*), leaving a 2(?) : 10-*dibromophenanthrene* (II):



This will probably be found to be a general reaction for compounds of this kind.

The preparation of the 9-bromo-derivative has been improved by Austin (T., 1908, **94**, 1762) by using carbon tetrachloride as a diluting medium. A systematic examination of the reaction in this diluent has been made by the author by using varying amounts of bromine. With two atoms Austin's results were confirmed. Three yielded 28 per cent. of the 9-bromo-derivative and 23 per cent. of 2(?)-bromophenanthrene dibromide, whilst four atoms gave 31 per cent. of the 9-bromo-derivative, together with 30 per cent. of 2(?)-bromophenanthrene dibromide, which decomposed to 23 per cent. of the 2(?):10-dibromo-derivative melting at 162°. The dibromo-derivative having the nearest melting point (158°) to this is that of Zetter (*loc. cit.*), but his is readily soluble in alcohol, and crystallises only in plates, whereas the new one is soluble in alcohol only on boiling, and crystallises most readily in needles, but is dimorphous and can also be obtained in plates.

The proof of the position of the bromine atom in position 10 is shown by the formation of a phenanthrone on oxidation. Normally, phenanthrene, or its compounds having the 9:10-positions unoccupied, yield *o*-quinones, but in this instance only one oxygen atom was found in the oxidised product, indicating that one of these positions was already occupied. The reaction may be represented thus:

$$\begin{array}{l} CH{=}CBr \\ C_6H_4{\cdot}C_6H_3Br \end{array} \longrightarrow \begin{array}{l} CO{-}CHBr \\ C_6H_4{\cdot}C_6H_3Br \end{array}$$

(III.)

The phenanthrone yielded a monoxime, but no dioxime, as would have been the case had the 9:10-positions been occupied by oxygen. Additional evidence was forthcoming on nitration, where exactly analogous conditions hold; a mononitrate, but no dinitrate, was obtained. It may therefore be concluded that position 10 is occupied by one of the bromine atoms.

In an attempt to prove the position of the second bromine atom the evidence was of a negative character. If we consider the positions 1, 2, 3, and 4 which it might occupy, number 3 is excluded, because Sandqvist (*loc. cit.*) describes a dibromophenanthrene melting at 143°, which he demonstrates to be the 10:3(or 6)-derivative. Of the remaining positions, 2 was chosen for attack. 2-Ethoxyphenanthrene was subjected to exactly the same conditions of experiment, in which the dibromo-derivative melting at 162° was formed. The sole product was the 10-bromo-2-ethoxyphenanthrene, so that when position 2 is occupied, the bromine enters the bridge only; from this it might be inferred that the second bromine atom

occupies position 2, but this evidence cannot be taken as conclusive, *and the matter is still under investigation.*

EXPERIMENTAL.

2(?)-*Bromophenanthrene Dibromide* (I).

A solution of 32 grams of dry phenanthrene in 50 c.c. of dry carbon tetrachloride was treated with 57·4 grams (4 atoms) of previously dried bromine in 50 c.c. of the same solvent. After forty-eight hours 11 grams of pale yellow crystals had formed, which were found to be 9:10-dibromophenanthrene. The filtrate was evaporated to dryness in a current of dry warm air, no heat being applied, when a yellow, crystalline solid remained. On extraction with three successive portions of cold light petroleum, part dissolved, leaving 10 grams of a pale yellow substance, which crystallised from glacial acetic acid in long, flat, lemon-yellow needles melting and decomposing at 100—102 (Found, Br=57·64. $C_{14}H_9Br_3$ requires Br=57·55 per cent.).

The bromine, evolved as hydrogen bromide, was estimated by heating to 110° and passing the gas into silver nitrate solution (Found, Br=18·79. $C_{14}H_9Br_3$(less HBr) requires Br=19·10 per cent.).

The compound can be boiled in glacial acetic acid solution without change, but it gradually decomposes into the dibromo-derivative and hydrogen bromide if exposed to a warm atmosphere.

2(?):10-*Dibromophenanthrene* (II).

After heating 10 grams of the preceding compound at 100° until all hydrogen bromide ceased to be evolved, it yielded 8 grams of a white solid, which crystallised from a concentrated solution in boiling alcohol in long, slender, colourless needles, forming throughout the liquid. On allowing the filtrate to remain, no needles appeared, but very small, colourless plates formed on the sides of the dish. These were again crystallised from a concentrated, boiling, alcoholic solution, when they separated in needles like the first crop. The needles (first crop), on the other hand, separated from a dilute solution in boiling alcohol in plates. The needles melted at 162°, the plates at 161° (Found [needles], C=50·00; H=2·68; Br=47·68; [*plates*], C=49·83; H=2·43. $C_{14}H_8Br_2$ *requires* C=50·00; H=2·35; Br=47·61 per cent.).

The plates were found to be triclinic, and the needles rectangular. The substance is therefore dimorphous. When kept for some months the needles gradually break down into plates.

2(?) : 10-*Dibromophenanthrene* is fairly readily soluble in glacial acetic acid, ether, acetone, chloroform, or benzene, less so in light petroleum or alcohol, and insoluble in water. The solubility of the plates in ether, acetone, or glacial acetic acid is slightly less than that of the needles, whilst the latter dissolve in alcohol rather less readily than the plates; in other solvents their solubilities are alike. Both plates and needles yield the same phenanthrone and the same nitro-compound.

2(?) : 10-*Dibromophenanthrone* (III).

Two grams of the above dibromo-derivative dissolved in 120 c.c. of glacial acetic acid were oxidised by heating for two hours with an equal weight of chromium trioxide. If the solution becomes cold, yellow crystals appear, but a better yield is obtained by cooling to about 30° and pouring into water. The precipitate (1·9 grams) crystallised from alcohol in slender, lemon-yellow needles melting at 203° (Found, C = 47·64; H = 2·50. $C_{14}H_8OBr_2$ requires C = 47·72; H = 2·27 per cent.).

The compound is not so soluble in alcohol, ether, or glacial acetic acid as in most of the other organic solvents. Analyses of the substance prepared from both the plates and needles of the dibromo-derivative gave concordant results. It dissolves in warm concentrated sulphuric acid with a dark, greenish-blue colour, and is reprecipitated on dilution with water.

The *monoxime* is readily formed by boiling for three hours a 1 per cent. alcoholic solution of the substance with two-fifths of its weight of hydroxylamine hydrochloride. After evaporating the alcohol, the residue is boiled for some minutes with water and is then left as a greenish-yellow powder, the yield being quantitative. It crystallises from benzene in bulky, dull yellow, hair-like crystals, which shrink considerably on drying, and melt and decompose at 239° (Found, N = 4·05; Br = 43·44. $C_{14}H_9ONBr_2$ requires N = 3·81; Br = 43·59 per cent.).

Although very readily soluble in ether, acetone, or alcohol it is insoluble in cold benzene. It does not form an anhydride when treated with alcoholic potassium hydroxide.

2(?) : 10-*Dibromo-9-nitrophenanthrene*, $\begin{matrix} C(NO_2){:}CBr \\ C_6H_4{-}{-}C_6H_3Br \end{matrix}$.

A 1 per cent. solution of 2(?) : 10-dibromophenanthrene in glacial acetic acid is heated to 60—70°, and then cold, fuming nitric acid added until a slight permanent cloudiness remains: the solution is

finally boiled for five minutes, and, on cooling, silky crystals (75 per cent. yield) are deposited, which separate from alcohol in lemon-yellow, feathery needles melting at 188° (Found, N=3·39. $C_{14}H_7O_2NBr_2$ requires N=3·61 per cent.).

The nitro-compound is very readily soluble in chloroform or benzene, but in acetone or alcohol only on boiling. On further addition of nitric acid or continued boiling of the mixture, no dinitro-derivative was formed, although several attempts were made to obtain this; therefore the bromine atom in position 10 is not readily displaceable by the nitro-group.

A similar type of compound, namely, 9-bromo-10-nitrophenanthrene, has been prepared by Schmidt and Ladner (*loc. cit.*).

2(?):10-*Dibromo-9-aminophenanthrene*, $\begin{matrix} C(NH_2)\cdot CBr \\ C_6H_4 \text{---} C_6H_3Br \end{matrix}$.

The reduction of the nitro-compound was effected by boiling for one hour with tin and hydrochloric acid. The amine was washed with hot water, dissolved in warm alcohol, and the solution filtered. On pouring this into much water, a brown, flocculent precipitate was obtained, which, when dry, was extracted with a little cold chloroform. The pale brown solid (35 per cent. yield) crystallised from dilute alcohol in colourless needles melting at 177° (Found, N=4·08. $C_{14}H_9NBr_2$ requires N=3·98 per cent.).

The substance is very readily soluble in the usual solvents except light petroleum, ether, or chloroform, although it does not crystallise readily from these. On prolonged exposure to light it gradually turns brown. It dissolves on boiling with dilute sulphuric acid, and, on cooling, flocculent crystals of the hydrogen sulphate appear.

The *acetyl* derivative was prepared by heating the amine with twenty times its weight of acetic anhydride at 130—140° for six hours. The cold solution was poured into water, and the resulting white, granular solid, after being washed with dilute sodium hydroxide solution and then with warm water, crystallised from boiling alcohol in colourless, flat, tetragonal plates melting at 202°. The yield was 80 per cent. of the theoretical (Found, C=48·81; H=3·01. $C_{16}H_{11}ONBr_2$ requires C=48·85; H=2·80 per cent.). It is very readily soluble in cold chloroform, but dissolves in ether or alcohol only on boiling.

Action of Alcoholic Potassium Hydroxide on 2(?):10-*Dibromophenanthrene.*

When the dibromo-compound (one-fifth of the weight of the potassium hydroxide) is gradually added to 10 per cent. alcoholic

potassium hydroxide and the solution boiled for four hours, the *liquid becomes reddish-purple and deposits a 90 per cent. yield of* a blood-red precipitate, which is insoluble in water and all the usual organic solvents, with the exception of carbon disulphide and benzene, in which it is sparingly soluble. It crystallises from the latter in small, brilliant scarlet needles, which do not melt below 350°. Its composition was not indicated by analysis (Found, C=52·27; H=3·03 per cent.).

It leaves no residue on burning, and is not acted on by strong acids or alkalis in the cold, but is decomposed by the former on boiling. It is oxidised by chromium trioxide, yielding a clear, yellow solution, which on neutralisation with sodium hydroxide gives a yellow precipitate. The product is therefore not a qninone, neither is the red substance. This is further shown by the fact that *neither gives an oxime. The scarlet substance contains bromine.* 9-Bromophenanthrene does not yield a red compound.

A Dibromo-hydrocarbon, $C_{17}H_{16}Br_2$.

The three portions of light petroleum extract from the bromination of phenanthrene (p. 57) were united and evaporated to dryness, *leaving a pale brown oil, which solidified after twenty-four* hours and crystallised from alcohol in pale yellow needles melting at 216° (Fouud, C=53·64; H=4·04. $C_{17}H_{16}Br_2$ requires C=53·68; H=4·21 per cent.).

The compound contains bromine, and is evidently a dibromo-derivative of a hydrocarbon, occurring as an impurity in the phenanthrene.

10-Bromo-2-ethoxyphenanthrene, $\begin{matrix} CH{=}CBr \\ | \quad\quad | \\ C_6H_4{\cdot}C_6H_3{\cdot}OEt \end{matrix}$

2-Ethoxyphenanthrene (T., 1906, **89**, 1527) was brominated under exactly the same conditions as when 2(?):10-dibromophenanthrene was *formed.* The product, when heated at 100°, evolved hydrogen bromide and left a yellowish-white mass, which crystallised from glacial acetic acid in small, colourless leaflets (81 per cent. yield), melting at *148—149°* (Found, *C=63·87*; H=4·72; Br=26·34. $C_{16}H_{13}OBr$ requires C=63·78; H=4·32; Br=26·57 per cent.). It is very readily soluble in the usual solvents except methyl alcohol and glacial acetic acid.

Since bromine attacks the 9 and 10 positions most readily, it is reasonable to suppose that these have been entered, and the fact that hydrogen bromide is evolved on heating the crude product

would substantiate this view, a 9:10-dibromide being first formed and decomposing into the above substance and hydrogen bromide, just as in the case of Hayduck's dibromide (*loc. cit.*). Further evidence is afforded by the fact that 9:10-dinitro-2-ethoxyphenanthrene is not attacked by bromine under the same experimental conditions.

9:10-*Dinitro-2-ethoxyphenanthrene*, $\begin{matrix} C(NO_2):C\cdot NO_2 \\ C_6H_4 — C_6H_3\cdot OEt \end{matrix}$.

The *dinitro*-compound was prepared by treating a 3 per cent. glacial acetic acid solution of the ether with fuming nitric acid until a permanent cloudiness appeared, and then adding a slight excess, boiling for fifteen minutes, and allowing to remain for twenty-four hours. On pouring into water the dinitro-compound was precipitated, and was dried at 105°. After extracting with a little cold benzene, the residue crystallised from the same boiling solvent in pale yellow, shining, rhombic prisms melting at 247° (Found, N = 9·66. $C_{16}H_2O_5N_2$ requires N = 9·46 per cent.).

It is readily soluble in chloroform, but not in carbon tetrachloride. It burns very easily with a small flash, leaving no residue.

The author wishes to express his thanks for grants from the Research Fund of the Chemical Society and from the Government Grant Committee of the Board of Trade, towards the cost of the materials used in the work.

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V.—*Studies in Emulsions. Part II. The Reversal of Phases by Electrolytes, and the Effects of Free Fatty Acids and Alkalis on Emulsion Equilibrium.*

By SHANTI SWARUPA BHATNAGAR.

THE study of the effects of electrolytes on emulsion equilibrium is undoubtedly of great importance for the elucidation of the mechanism of emulsification, but unfortunately very little quantitative data is available on the subject. The work of Clowes (*J. Physical Chem.*, 1916, **20**, 445) is restricted to a particular type

of emulsion, in which the volumes of the two phases are always equal. In a previous paper (T., 1920, **117**, 549), this work of Clowes has been discussed. Subsequent work on the problem has shown that the procedure of using alkaline solutions and free fatty acids in oils employed by Clowes is not quite satisfactory. When dilute solutions of alkalis are used, a comparatively large amount of free fatty acid in the system is left unneutralised.

The presence of free fatty acid or free alkali makes the system more complex. In addition, they seem to have a definite effect on the emulsion equilibrium, as will be showu later. Really comparable results can only be obtained and repeated by employing neutral oil and soap solutions.

EXPERIMENTAL.

In all experiments described in this paper, various soaps were used instead of different alkalis. Sodium oleate and potassium stearate were obtained from Kahlbaum. The lithium stearate was a sample prepared by Sir William Ramsay, and preserved in this laboratory. Sodium linoleate and other soaps were prepared in the manner advocated by MacBain (*Trans. Faraday Soc.*, 1913, **9**, 99). The electrolytes were pure chemical reagents (excepting nickel nitrate), and were recrystallised before making up the solutions.

In order to ensure identical conditions for repeating the observations, the time for shaking, the volume of the phases, and the size and other conditions of vessel were always kept alike. It was found that under these conditions, with carefully cleansed vessels, the observations could be repeated with a fair degree of accuracy. The emulsions were prepared in wide-mouthed bottes, and the type noted by examining small portions of emulsions in a T-shaped glass container, according to the method described in a previous paper (*loc. cit.*), and with frequent testings under the microscope. The two methods gave identical results for all fine-grained emulsions.

Experiments with Electrolytes.

Volume of oil phase = 10 c.c.
Volume of aqueous phase = 10 c.c.
R_1 = Inversion point.

TABLE I.

Soap Used: Sodium Oleate.

The figures given in the columns represent the amount of the respective salts in millimols at R_1.

Amount of soap in millimol.	$Ba(NO_3)_2$.	$Sr(NO_3)_2$.	$Pb(NO_3)_2$.	$Ni(NO_3)_2$.	$Al_2(SO_4)_3$.	$Cr_2(SO_4)_3$.
0·080	0·0398	0·0398	0·0396	0·036	0·014	0·016
0·101	0·0500	0·052	0·504	0·040	0·017	0·019
0·150	0·080	0·084	0·082	0·060	0·025	0·027
0·162	0·084	0·090	0·088	0·076	0·027	0·030
0·210	0·112	0·116	0·110	0·0798	0·036	0·039

TABLE II.

Soap: Potassium Stearate.

Soap in millimol.	$Ba(NO_3)_2$.	$Sr(NO_3)_2$.	$Ni(NO_3)_2$.	$Pb(NO_3)_2$.	$Al_2(SO_4)_3$.	$Cr_2(SO_4)_3$.
0·086	0·044	0·046	0·040	0·040	0·018	0·018
0·10	0·0508	0·0512	0·050	0·052	0·026	0·022
0·15	0·084	0·086	0·078	0·088	0·027	0·026
0·25	0·132	0·136	0·128	0·140	0·048	0·048
0·30	0·156	0·160	0·150	0·154	0·056	0·057

TABLE III.

Soap: Lithium Stearate.

Soap.	$Ba(NO_3)_2$.	$Sr(NO_3)_2$.	$Ni(NO_3)_2$.	$Pb(NO_3)_2$.	$Al_2(SO_4)_3$.	$Cr_2(SO_4)_3$.
0·09	0·040	0·040	0·036	0·042	0·015	0·016
0·12	0·058	0·058	0·050	0·056	0·021	0·023
0·16	0·090	0·094	0·080	0·094	0·028	0·029
0·20	0·102	0·104	0·096	0·106	0·03	0·032

TABLE IV.

Soap: Sodium Linoleate.

Soap.	$Ba(NO_3)_2$.	$Sr(NO_3)_2$.	$Ni(NO_3)_2$.	$Pb(NO_3)_2$.	$Al_2(SO_4)_3$.	$Cr(SO_4)_3$.
0·083	0·068	0·068	0·058	0·072	0·028	0·028
0·112	0·100	0·106	0·090	0·116	0·038	0·037
0·125	0·128	0·134	0·120	0·136	0·042	0·043
0·18	0·198	0·20	0·178	0·200	0·061	0·063

The results shown in tables I, II, III, and IV indicate in a marked manner the difference in the amounts of various electrolytes required to bring about the reversal of phases. The effect of the valency of the electrolyte is worth noting. The amounts of the tervalent electrolytes, aluminium and chromium sulphates, required to bring about the reversal of phases are less than those

of bivalent electrolytes. The power of reversing the phases i these electrolytes is in the order: aluminium>chromium> nickel>lead>barium>strontium. Calcium, bivalent iron, an magnesium are found to have practically the same values a strontium, and are therefore not shown in the tables. The amoun of electrolytes required to bring about the reversal of phases differ with different soaps, but the valency effect of the electrolyte stil holds good.

Effect of Changing the Volume-ratio of the Phases.

In all previous experiments, the volumes of the oil and aqueo phases have been equal. Keeping all other conditions constan some experiments were tried in order to find how the action electrolytes on the inversion point is affected by changing th volume-ratio of the two phases. The results are shown in table V

TABLE V.

Total volume of emulsion always 20 *c.c.*

Soap: Lithium Stearate, 0·12 *millimol.*

B. P. paraffin in c.c.	Aqueous phase in c.c.	$Ba(NO_3)_2$ in millimol in the aqueous phase at R_1.	$Al_2(SO_4)_3$ in millimol at R_1.
2	18	0·078	0·030
5	15	0·070	0·028
8	12	0·060	0·024
10	10	0·058	0·021
11	9	0·054	0·018
13	7	0·044	0·012
15	5	0·040	0·010

It is interesting to note that the amount of multivalent elect lyte required to bring about the inversion of phases increases the volume of the aqueous phase is increased and diminishes as is reduced. A corresponding increase in the oil phase has a reve effect. Thus in table V the ratio between lithium stearate a barium chloride at the inversion point was as 0·24 : 0·058 when t volumes of the two phases were as 10 : 10. When the volume the aqueous phase was increased so that the ratio between th was 15 : 5, the amount of barium nitrate at R_1 increased to 0·0 millimol, and was reduced to 0·04 when the ratio became 5 : that is, on proportionately increasing the oil phase. Simi results were obtainable with other soaps and electrolytes used this investigation.

Effect of Dilution on the Reversal of Phases by Electrolytes.

Emulsions can be diluted infinitely by the addition of the continuous phase. It was considered desirable to find how dilution affects the action of electrolytes on the inversion point. A large quantity of fine-grained emulsions was prepared by vigorously shaking in a mechanical shaker some oil to which the aqueous phase was gradually added until the total volumes of the aqueous and oil phases became equal. This standard emulsion was divided into four equal portions of 20 c.c. each. One portion was kept undiluted, and the other three portions were differently diluted with solutions of soap and different amounts of electrolytes added previous to a second shaking, in the manner already described. Some of the results are given in table VI.

TABLE VI.

Soap: Sodium Oleate.

Amount of sodium oleate in each sample, 0·101 millimol.

20 c.c. of emulsion.	$BaCl_2$ in millimol at the inversion point.	$Al_2(SO_4)_3$ in millimol at the inversion point.
1. Standard emulsion	0·050	0·014
2. ,, ,, twice diluted	0·0798	0·025
3. ,, ,, thrice diluted......	0·112	0·040
4. ,, ,, four times diluted	0·156	0·057

The results in table VI indicate that the greater the dilution or the distance between the oil particles in an emulsion, the larger is the amount of the multivalent electrolyte required to bring about the reversal of phases. These results are in keeping with the previously observed effect of dilution on the rate of coagulation of colloidal sols by electrolytes (T., 1919, **115**, 462).

A few observations were also made to ascertain how the rate of coagulation of the typical natural emulsion, milk, is affected on dilution. The procedure consisted in preparing several different solutions of milk and water. Equal volumes of these solutions were placed in clean test-tubes, a definite volume of 0·4906*N*-sulphuric acid was added, the tube well shaken, and the times for the first perceptible change and complete coagulation were noted. Table VII indicates some of the results obtained.

TABLE VII.

Volume of solution always 20 c.c.	Time for first perceptible change on the addition of a known volume of sulphuric acid.
Pure milk	Immediately after adding.
Twice diluted	9 minutes 2 seconds.
Thrice diluted	12 minutes.
Four times diluted	15 minutes 3 seconds.
Five times diluted	25 minutes 2 seconds.
Eight times diluted	50 minutes.
Ten times diluted	70 minutes.

Another set of experiments was performed to find the strength of a known volume of acid which will produce a perceptible change immediately on addition to the solutions, and it was found that the greater the dilution, the stronger was the acid required to produce an immediate coagulation effect. It is thus evident that the reversal of phases by electrolytes in emulsions, the precipitation of colloidal sols in suspensions, and the coagulation of substances like milk, in which the acids used act on the casein membrane round the fat globules, are similarly affected on dilution. It is probable that the cause or causes producing these identical effects are also identical, and a thorough study of any one of these phenomena may lead to the elucidation of the problem of coagulation.

Effects of Free Fatty Acids and Alkalis on the Emulsion Equilibrium.

The procedure adopted for investigating the irregularities observed when free fatty acids and alkalis were used for emulsification consisted in preparing three sets of emulsions. All contained the same amount of sodium oleate and the same volume ratio, the only difference being that in one set the oil contained free fatty acid, in the second the aqueous phase contained free alkali, and in the third set neutral oil and soap solutions alone were used. The following table represents the results, which show

TABLE VIII.

Soap Used: Sodium Oleate.

Emulsions containing 0·162 millimol of soap.	Free potassium hydroxide. Gram.	Free fatty acid. Gram.	$Ba(NO_3)_2$ in millimol required at R_1.
20 c.c.	0·01	0	0·09
"	0·021	0	0·096
"	0	0·003	0·078
"	0	0·008	0·070
"	0	0	0·084

that the free fatty acids and free alkalis shift the inversion point in opposite directions.

During the microscopic examination of these three sets of emulsions, it was found that the average size of globules of oil was greater in emulsions containing free fatty acid and smaller in emulsions containing free alkali in the system than the average size for identical and equal shakings when neutral oil and soap solutions alone were used. It is interesting to note that the addition of a little free alkali to a soap solution also decreases the size of the particles, and results in turning a slightly turbid solution into a perfectly clear one, whilst the addition of free fatty acid increases the size of the particles and makes the solution more turbid. This may possibly account for the difference in the sizes of particles in the above-mentioned emulsions.

It is to be noted that as the degree of dispersion is an important factor in the stability of an emulsion, all attempts to arrange various emulsifying agents in order of their efficiency for emulsification, without taking into account the size of the particles of these agents, are defective. The size of the particles of an emulsifying agent has also been found by Pickering (T., 1907, **91**, 2001) to have a definite effect on the degree of dispersion.

Discussion of Results.

The results indicated in tables I, II, III, and IV show that the tervalent electrolytes have a greater effect on the inversion of the emulsion than the bivalent ones. A similar conclusion has been drawn by Clowes (*loc. cit.*). The effect of dilution and of increasing the distance between the oil particles in an emulsion is essentially similar in nature to the effect of dilution on colloidal sols. A complete discussion of the results obtained here will be reserved for a later contribution.

The difference in the amount of electrolytes required to bring about the reversal of phases with different soaps points to the probability of a difference in their protective actions. The results indicate that the soaps can be arranged in order of their protective action, as potassium stearate>sodium stearate>sodium and potassium palmitates>potassium oleate>sodium oleate, for B.P. paraffin oil. The results have an important bearing on the cleansing power of soaps. The old hypothesis of Chevreul, that the cleansing power of soap is due to the free alkali liberated, is now discarded. The modern conception attributes the washing power of soap to its "emulsifying efficiency" and to its protective action, which keeps the dirt and grease bound in the form of an

emulsion. *On this view, the cleansing properties of soaps will be* considerably affected by the electrolytic impurities in water. Sodium linoleate and soaps with a little free alkali will be good for cleansing purposes, as they give finer-grained emulsions than the sodium oleate solutions when pure water is employed for washing. Large amounts of calcium or barium salts, or salts of tervalent metals, in water will be injurious in these cases, as well as when neutral or acid soap solutions are employed, for the latter are also easily transformed into water-in-oil emulsions, which are very sticky and difficult to remove by water.

It is intended to study the various physical properties, particularly viscosities, of emulsions of two immiscible liquids of equal densities, in order to obtain more evidence as to the mechanism of the reversal of phases in emulsions, and further work on the renewal of phases in emulsions prepared by insoluble emulsifiers is in progress.

Summary.

(1) It has been shown that tervalent electrolytes are more effective in bringing about the reversal of phases than bivalent ones.

(2) Soaps and electrolytes have been arranged in the order of their emulsifying and precipitating powers, respectively, for B.P. paraffin oil emulsions.

(3) It has been shown that the reversal of phases in emulsions, the precipitation of sols in suspensions, and the coagulation of natural emulsions like milk, are similarly affected by dilution.

(4) The bearing of the results on the chemical interpretation of the washing power of soap is briefly discussed.

(5) The effects of free alkalis and free fatty acids on soap emulsions have been investigated.

The author takes this opportunity of thanking Prof. F. G. Donnan, F.R.S., for the help afforded him during this investigation. His thanks are also due to Dr. J. C. Ghosh and Mr. J. N. Mukherjee.

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[*Received, October 12th*, 1920.]

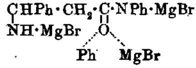
VI.—*β-Amino-β-phenylpropiophenone.*

By ALEX. MCKENZIE and FRED BARROW.

α-AMINO-KETONES, for example, α-aminopropiophenone, exhibit great instability in the free state on account of their tendency to condense in the presence of air to give substituted pyrazines (Gabriel, *Ber.*, 1908, **41**, 1127). On the other hand, β-amino-ketones are much more stable; diacetoneamine is exceptional, as it can even be distilled, but other ketones of this class are not nearly so stable; thus Gabriel (*Ber.*, 1908, **41**, 242) has shown that β-aminopropiophenone evolves ammonia when heated with aqueous potassium hydroxide, and it does not appear from his description that the compound is stable enough to be kept at the ordinary temperature for any length of time.

For the purpose of another research it was desired to obtain a β-amino-ketone containing an asymmetric carbon atom, and the preparation of β-amino-β-phenylpropiophenone was accordingly undertaken by the authors in the hope that this compound would be sufficiently stable to permit of its isolation. The preparation was carried out as follows. Cinnamic acid was converted into β-amino-β-phenylpropionic acid, from which the corresponding *phthalimino-acid* was obtained by heating with phthalic anhydride. The action of benzene and aluminium chloride on the chloride of the phthalimino-acid led to *β-phthalimino-β-phenylpropiophenone*, which was converted by means of aqueous alkali into the corresponding *phthalamic acid* (compare Gabriel, *Ber.*, 1908, **41**, 242, 513, and other papers by the same author). The hydrolysis of the phthalamic acid was accomplished by a mixture of glacial acetic acid and concentrated hydrochloric acid. The resulting hydrochloride on decomposition with ammonia gave *β-amino-β-phenylpropiophenone* as a solid melting at 82—83°. The free amino-ketone is much more stable at the ordinary temperature than is desylamine, the related α-amino-ketone.

An attempt was made to obtain the ketone by a more direct method, namely, by the action of magnesium phenyl bromide on *β-amino-β-phenylpropionanilide*, $NH_2 \cdot CHPh \cdot CH_2 \cdot CO \cdot NHPh$. The disruption of the additive compound by aqueous ammonium chloride led, however, to the regeneration of the anilide. The result would suggest that the additive compound may have been



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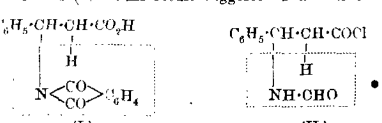
in which case the rearrangement into a product giving the aminoketone on hydrolysis did not occur. Now it has been found by McKenzie, Martin, and Rule (T., 1914, **105**, 1583) that the action of Grignard reagents on alkylated acid amides (for example, *r*-mandeloethylamide and *l*-β-hydroxy-β-phenylpropionethylamide) does not always lead to the formation of the corresponding ketols, and it seems probable that the additive compounds formed in those cases may also have been of the oxonium type postulated above. v. Braun has, in fact, suggested the structure $\frac{R_2N}{R}>C{:}O<\frac{MgHlg}{R'}$ for the compounds obtained from dialkylated amides. The recent work of v. Braun, Heider and Müller (*Ber.*, 1917, **50**, 1637) and of v. Braun and Kirschbaum (*Ber.*, 1919, [*B*], **52**, 1725) on the action of Grignard reagents (prepared from bromoalkylated anilines) on aldehydes and ketones respectively certainly lends support to the view that the first phase in the addition of a Grignard reagent to an aldehyde or a ketone consists in the formation of an oxonium compound where the reagent attaches itself to the oxygen atom of the carbonyl group of the aldehyde or ketone. Such an additive compound would be labile enough to undergo, as a general rule, isomeric change with readiness prior to its hydrolysis, but apparently it may sometimes happen that this rearrangement does not occur.

The action of aluminium chloride on a solution of β-formylamino-β-phenylpropionyl chloride in benzene took an unexpected course, the product being ββ-diphenylpropiophenone. Now it is shown in the present paper that β-phthalimino-β-phenylpropionic acid decomposes on heating into carbon dioxide, phthalimide, cinnamic acid, and styrene, the last-named substance being doubtless formed from the cinnamic acid (I). This result suggested a similar course for



(I.) (II.)

the decomposition of β-formylamino-β-phenylpropionyl chloride into formamide and cinnamoyl chloride (II), aluminium chloride acting as a catalyst. The cinnamoyl chloride formed in this manner then reacts with benzene and aluminium chloride with the formation of ββ-diphenylpropiophenone. The interaction of cinnamoyl chloride, benzene, and aluminium chloride, under the conditions described in

the experimental part, gave a mixture of ββ-diphenylpropiophenone and *ββ-diphenylpropionic acid.*

β-Benzoylamino-β-phenylpropionyl chloride differed from the formyl compound inasmuch as it underwent the normal reaction with benzene and aluminium chloride, the product being *β-benzoylamino-β-phenylpropiophenone.*

Some optically active derivatives of β-amino-β-phenylpropionic acid are at present under investigation by one of us (A. McK.).

EXPERIMENTAL.

β-Amino-β-phenylpropionanilide.

β-Amino-β-phenylpropionic acid was prepared by the action of hydroxylamine on cinnamic acid according to Posner's method (*Ber.*, 1905, **38**, 2316). Four grams of the well-dried and finely-powdered amino-acid were suspended in 20 c.c. of freshly-distilled acetyl chloride, the mixture was cooled in ice, and treated gradually with 5·3 grams of finely-powdered phosphorus pentachloride. The mixture was shaken during the addition of the pentachloride (fifteen minutes), and the shaking was continued for half an hour longer at the ordinary temperature. The resulting solid, β-amino-β-phenylpropionyl chloride hydrochloride, was separated and washed with acetyl chloride and light petroleum. A solution of 2·5 grams of it were suspended in dry ether, and treated at the ordinary temperature with a solution of 4·2 grams of aniline in ether. Water was then added, the aqueous solution separated, and made alkaline with sodium hydroxide. The anilide precipitated was crystallised from aqueous alcohol (Found, C = 74·8; H = 6·9. $C_{15}H_{16}ON_2$ requires C = 75·0; H = 6·7 per cent.).

β-Amino-β-phenylpropionanilide, $NH_2 \cdot CHPh \cdot CH_2 \cdot CO \cdot NHPh$, separates from ethyl alcohol in colourless plates melting at 122°. It is readily soluble in ethyl alcohol or chloroform, moderately so in benzene or ether, and sparingly so in light petroleum.

Attempts to prepare the amide and the piperidide of β-amino-β-phenylpropionic acid by the action of dry ammonia and of piperidine on a suspension of the chloride hydrochloride in dry ethereal solution gave amorphous products, probably due to polypeptide formation.

The anilide (1 mol.) was subjected to the action of magnesium phenyl bromide (6 mols.). On decomposing the additive compound with ammonium chloride the anilide was regenerated.

Action of β-Formylamino-β-phenylpropionyl Chloride on Benzene in the Presence of Aluminium Chloride.

The formylation of the amino-acid was carried out as described by Fischer, Scheibler, and Groh (*Ber.*, 1910, **43**, 2020), and the formyl acid then converted into its chloride by means of acetyl chloride and phosphorus pentachloride. The chloride, prepared from 3·9 grams of the formyl acid, was a viscid, yellow oil; it was dissolved in 50 c.c. of benzene, and acted on by 5 grams of aluminium chloride by heating on the water-bath for one hour. After decomposition with hydrochloric acid and removal of the benzene, the product was crystallised twice from ethyl alcohol, when lustrous needles (0·7 gram) separated. These melted at 94—95°, contained no nitrogen, and consisted of ββ-diphenylpropiophenone, $CHPh_2{\cdot}CH_2{\cdot}COPh$ (Found, C=88·1; H=6·5. Calc., C=88·1; H=6·3 per cent.). Kohler (*Amer. Chem. J.*, 1903, **29**, 352) gives m. p. 96°.

Action of Cinnamoyl Chloride on Benzene in the Presence of Aluminium Chloride.

This action had already been investigated by Kohler, Heritage, and Burnley (*Amer. Chem. J.*, 1910, **44**, 60) under somewhat different conditions to those employed by us. They found that ββ-diphenylpropiophenone was accompanied by 3-keto-1-phenyl-2:3-dihydroindene and β-chloro-β-phenylpropiophenone. The product obtained under the following conditions appeared to consist entirely of ββ-diphenylpropionic acid and ββ-diphenylpropiophenone.

A mixture of 10 grams of cinnamic acid and 14·8 grams of phosphorus pentachloride was heated on the water-bath for half an hour, the oxychloride removed under diminished pressure, and the resulting oil acted on by 50 c.c. of benzene and 10 grams of aluminium chloride. The action was completed by heating, and the mixture allowed to remain overnight. Dilute hydrochloric acid was added, the product extracted with ether, and the ethereal solution then shaken with sodium carbonate. On acidifying the alkaline extract with hydrochloric acid, 5·1 grams of ββ-diphenylpropionic acid were precipitated, which after crystallisation from ethyl alcohol separated in lustrous, white needles melting at 149—150°. Liebermann and Hartmann (*Ber.*, 1892, **25**, 2124), who obtained the acid as one of the products of the action of sulphuric acid on cinnamic acid and benzene, give m. p. 149°. (Equivalent=229·1. Calc.=226.)

After being dried with sodium sulphate, the ethereal solution on evaporation gave a red oil which solidified almost completely when

kept in the ice-chest for two days. The solid was freed from a small quantity of oil and purified by crystallisation from alcohol. It amounted to 11·5 grams, and consisted of ββ-diphenylpropiophenone.

β-Benzoylamino-β-phenylpropiophenone.

β-Amino-β-phenylpropionic acid was converted into its benzoyl derivative, which melted at 194—195°, whereas Posner (*loc. cit.*) gives 194—196°. Ten grams of the benzoylamino-acid were converted by means of acetyl chloride and phosphorus pentachloride into β-benzoylamino-β-phenylpropionyl chloride, which crystallises in needles. The latter was dissolved in 50 c.c. of benzene, and acted on by 10 grams of aluminium chloride. After the usual manipulation, 4·1 grams of a solid were isolated.

β-Benzoylamino-β-phenylpropiophenone,

$$NHBz{\cdot}CHPh{\cdot}CH_2{\cdot}COPh,$$

separates from ethyl alcohol in lustrous, slender, colourless needles melting at 152—154° (Found, C = 79·9; H = 6·1; N = 4·3. $C_{22}H_{19}O_2N$ requires C = 80·2; H = 5·8; N = 4·3 per cent.).

β-Phthalimino-β-phenylpropionic Acid.

A mixture of 11 grams of β-amino-β-phenylpropionic acid and 10·5 grams of phthalic anhydride were heated for two hours at 155—165°, at the end of which time the phthalimino-acid commenced to crystallise from the molten mass. On cooling, the acid was dissolved in 20 c.c. of hot glacial acetic acid, and 20 c.c. of benzene were added. On cooling, 13 grams of the crude acid separated. Purification was effected by crystallisation from benzene.

β-Phthalimino-β-phenylpropionic acid,

$$C_6H_4{:}(CO)_2{:}N{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H,$$

melts at 169·5—170·5°, is very readily soluble in hot ethyl alcohol or hot glacial acetic acid, moderately so in benzene, and very sparingly soluble in hot water. It separated from alcohol in slender needles (Found, C = 69·1; H = 4·7. $C_{17}H_{13}O_4N$ requires C = 69·1; H = 4·4 per cent.).

In a second preparation 35 grams of phthalic anhydride and 36 grams of the amino-acid gave 48 grams of the phthalimino-acid melting at 168—170° after one crystallisation from a mixture of 60 c.c. of glacial acetic acid and 60 c.c. of benzene.

The *acid chloride*, prepared by heating the acid with an excess of thionyl chloride for half an hour, separates from benzene in needles melting at 96—97°. For analysis it was dried over phos-

phoric oxide and paraffin wax (Found, Cl = 10·6. $C_{17}H_{12}O_3NCl$ requires 11·3 per cent.).

The *anilide*, prepared by the interaction at the ordinary temperature of aniline and the acid chloride in ethereal solution, separates from glacial acetic acid in glistening prisms or rhomboidal plates melting at 238°. It is sparingly soluble in ethyl alcohol (Found, N = 7·5. $C_{23}H_{18}O_3N_2$ requires N = 7·6 per cent.).

The *methyl* ester, prepared by the esterification of the acid with methyl alcohol and hydrogen chloride, separates from ethyl alcohol in plates melting at 92° (Found, N = 4·9. $C_{18}H_{15}O_4N$ requires N = 4·5 per cent.).

The action of heat on β-phthalimino-β-phenylpropionic acid was studied. Evolution of carbon dioxide began at 240° and became vigorous at 300°. The temperature was maintained at 320—350° for half an hour. The liquid, which had a pronounced odour of styrene, was then distilled under ordinary pressure. The residue was dissolved in ethyl alcohol and decolorised with charcoal; phthalimide was isolated from it. The distillate solidified to a white, crystalline mass, which was crystallised twice from a mixture of ethyl alcohol and benzene; the product was identified as phthalimide. The alcohol–benzene solution from which the phthalimide had been separated was extracted with aqueous sodium carbonate, and cinnamic acid was obtained from the alkaline solution by acidification and extraction with ether.

β-Phthalimino-β-phenylpropiophenone.

The best conditions for the preparation of this compound were the following. Twenty-five grams of the phthalimino-acid were heated for half an hour on the water-bath with 20 grams of thionyl chloride until the evolution of hydrogen chloride ceased. The excess of thionyl chloride was removed by distillation under diminished pressure, when the acid chloride remained as a very viscid, yellow oil Benzene (100 c.c.) was added to the warm oil, the greater part of which dissolved and, on cooling, separated in a mass of needles. Aluminium chloride (20 grams) was then added. Action soon started with evolution of hydrogen chloride. After remaining at the ordinary temperature overnight, the mixture was heated for twenty minutes, when a further vigorous evolution of hydrogen chloride took place. On cooling, water and hydrochloric acid were added, and the benzene removed by distillation in a current of steam. The ketone was left as a viscid, pale yellow oil, which solidified readily. It was separated and crystallised from ethyl alcohol. Yield, 26 grams.

β-Phthalimino-β-phenylpropiophenone,

$C_6H_4{:}C_2O_2{:}N{\cdot}CHPh{\cdot}CH_2{\cdot}COPh$,

separates from ethyl alcohol in needles melting at 116—117°. It is readily soluble in hot alcohol, but only moderately so in the cold solvent. It crystallises sluggishly, and tends to separate from hot concentrated solutions as an oil.

β-Benzoyl-α-phenylethylphthalamic Acid.

β-Phthalimino-β-phenylpropiophenone (7·5 grams) was suspended in 20 c.c. of ethyl alcohol, and heated on the water bath for ten minutes with 30 c.c. of *N*-sodium hydroxide. The solution was diluted with 200 c.c. of water and acidified with hydrochloric acid. The phthalamic acid was precipitated as an oil, which on stirring coagulated to form a pasty mass, and this on remaining overnight became quite solid and friable. It was purified by crystallisation from ethyl alcohol.

β-Benzoyl-α-phenylethylphthalamic acid,

$COPh{\cdot}CH_2{\cdot}CHPh{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$,

separates from ethyl alcohol in needles melting at 132° (Found, N=3·7. $C_{23}H_{19}O_4N$ requires 3·8 per cent.). It is readily soluble in acetone, ethyl alcohol, or glacial acetic acid, moderately so in benzene, and sparingly soluble in light petroleum.

β-Amino-β-phenylpropiophenone.

A solution of 10 grams of β-benzoyl-α-phenylethylphthalamic acid in 50 c.c. of hot glacial acetic acid was heated on the water-bath for one hour with 30 c.c. of concentrated hydrochloric acid; a small amount of a pale yellow oil separated on heating. On the addition of 150 c.c. of water a further quantity of oil was precipitated, which became pasty on shaking. The clear solution was separated and evaporated to about 50 c.c. under diminished pressure, separated from a further small quantity of oil, and finally evaporated to dryness under diminished pressure. The amino-ketone hydrochloride was obtained in this way in slender, colourless needles accompanied by a small amount of a viscid, yellow oil. The aqueous solution was extracted with ether and rendered alkaline with ammonia. The precipitated amino-ketone was extracted with ether, the ethereal solution dried with sodium sulphate, and the ether removed. The residual pale yellow oil solidified on cooling and was crystallised from a mixture of benzene and light petroleum. The yield was 0·75 gram.

β-Amino-β-phenylpropiophenone, $NH_2{\cdot}CHPh{\cdot}CH_2{\cdot}COPh$, crys-

tallises in soft, colourless leaflets melting at 82—83° (Found, N = 6·3. $C_{15}H_{15}ON$ requires N = 6·2 per cent.). It is readily soluble in ethyl alcohol, benzene, ether, or ethyl acetate, and only sparingly so in cold light petroleum (b. p. 30—50°).

It is moderately stable, differing in this respect markedly from desylamine; thus a specimen kept in a well-corked tube underwent no apparent change when kept for six days. It then became yellow, the crystals adhered together, and after a further four to five days it was transformed into a yellowish-brown, semi-liquid mass.

In another preparation where 15 grams of the phthalamic acid were hydrolysed by heating for half an hour with 60 c.c. of hydrochloric acid and 100 c.c. of glacial acetic acid, the yield of aminoketone (2·5 grams) was better than in the experiment just described.

The *picrate* crystallises from ethyl alcohol in yellow leaflets (Found, N = 12·4. $C_{15}H_{15}ON,C_6H_3O_7N_3$ requires N = 12·3 per cent.), which commence to darken and sinter at 175°, and melt and decompose at 193°.

The *platinichloride* separates from dilute hydrochloric acid in brown needles (Found, Pt = 22·5. $(C_{15}H_{15}ON)_2H_2PtCl_6$ requires Pt = 22·7 per cent.). It shows no definite melting point, but commences to darken and shrink to a thin core at 195°, decomposition being complete at 250°.

The crude β-amino-β-phenylpropiophenone hydrochloride resulting from the hydrolysis of the phthalamic acid was shaken with benzoyl chloride and sodium hydroxide. The resulting solid was crystallised from ethyl alcohol, from which it separated in needles melting at 152—153°. This was identical with the benzoyl derivative previously described (p. 73) obtained by the interaction of β-benzoylamino-β-phenylpropionyl chloride and benzene in the presence of aluminium chloride.

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[*Received, December 17th*, 1920.]

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VII.—*The Methylation of Cellulose. Part III. Homogeneity of Product and Limit of Methylation.*

By William Smith Denham.

In previous papers (Denham and Woodhouse, T., 1913, **103**, 1735; 1914, **105**, 2357; 1917, **111**, 244), the methylation of cellulose and of starch was announced, and some results were communicated of an investigation on the methyl ethers of cellulose and their hydrolytic products. The latter include a well-defined, crystalline trimethyl glucose, to which a constitutional formula has been assigned. Immediate aims in the development of this research have been the preparation of a methyl ether of maximum methoxyl content, in which the cellulose complex shall have undergone the minimum of degradation, and the examination of the limiting and intermediate ethers and their degradation products. It is proposed to amplify and discuss in a subsequent communication the additional results now presented.

For the preparation of a highly methylated cellulose, the method already described, namely, the treatment with methyl sulphate of cotton which has been soaked in a solution of sodium hydroxide, was found to be the most successful, and repetitions of this process, variously modified, have yielded a product containing 44·6 per cent. of methoxyl. This value approximates to the 45·6 per cent. of methoxyl required by theory for trimethyl cellulose. The slow rate of increase in the methoxyl content during the final stages of the methylation, itself an indication that the limit has been nearly approached, has rendered advisable the additional observations now in progress before the limit can be definitely announced. That these ethers retain a high degree of complexity is indicated by the almost complete absence of copper-reducing property in a product containing about 40 per cent. of methoxyl, in which, as in more highly methylated preparations, the fibrous structure of cellulose persists. Further, the displacement of hydrogen by methyl groups does not confer solubility in such solvents as alcohol, acetone, or chloroform.

The solubility of methylated cellulose in Schweitzer's reagent, on the other hand, appears to decrease as the methoxyl content increases, and products which contain about 40 per cent. of methoxyl are insoluble. The question of the homogeneity of methylated cellulose is of great importance in relation to deductions regarding the constitution of cellulose from the nature

of the hydrolytic products, and some experiments which give information on this point may therefore be referred to, although they were made primarily to ascertain whether, by the restricted action of Schweitzer's reagent especially on preparations of low average methoxyl content, a highly methylated portion could be separated to serve as a convenient source of the crystalline trimethyl glucose. It was found that several preparations of methyl cellulose, when treated with Schweitzer's reagent so that only a part was dissolved, yielded a residue with a methoxyl content greater than that of the untreated substance. The degree of heterogeneity thus revealed depends, as might be expected, on the manner of preparation of the methyl cellulose; for material of low average methoxyl content, it was greatest where concentrated alkali had been employed, possibly owing to an unequal penetration of the cotton by the alkali. The most homogeneous product of those examined was one in the preparation of which an ethereal solution of methyl sulphate was employed, and it may be noted that the best yields, apparent in an increased weight of material after methylation, were obtained when ether was present. A preparation containing about 40 per cent. of methoxyl gave indications of lack of uniformity explicable from its history; one containing 42 per cent. of methoxyl was quite insoluble in Schweitzer's reagent, and in alcohol, acetone, or chloroform, and is therefore so far homogeneous.

A comparison of the history of the sample of methylated cellulose which yielded the hydrolytic products, already described and discussed (T., 1914, **105**, 2357), with the histories of the preparations made without ether, which were examined by means of Schweitzer's reagent, indicates a superior uniformity in the earlier product, as in the later ones there were fewer stages in the methylation. It is thus probable that the trimethyl glucose was derived, not from a small proportion of highly methylated substance, but from a more general distribution of trimethyl glucose residues in the cellulose complex.

As the limit is approached, irregularities in methylation will be smoothed out, but the question of yield remains. The loss of material due to chemical action need not be great. In one series, 100 grams of cotton gave 104 grams of methyl cellulose containing 31·3 per cent. of methoxyl, the yield being thus 91 per cent. of the theoretical; the product had undergone four treatments, that is, it had been soaked in alkali, treated with methyl sulphate, and washed and dried four times, so that at least a part of the loss was mechanical. Owing to losses due to mishaps, the yields have not been followed continuously to the highest degree of methylation attained*: the loss is small, however, from stage to stage, and

is usually quite clearly mechanical loss sustained in manipulation.

The conclusions seem to be justified that the limit of methylation of cellulose lies in the neighbourhood of that required for trimethyl cellulose, and that a methyl cellulose of this limiting methoxyl content can be prepared which is representative of the whole of the original cellulose. The further investigation of these questions and of the fission products of methyl cellulose is in progress.

EXPERIMENTAL.

The following examples illustrate the yields obtained in several preparations of methyl cellulose and the behaviour of the products towards Schweitzer's reagent.

I. *Methyl Cellulose containing* 20·4 *per cent. of Methoxyl.*—The solution of sodium hydroxide employed contained 20 grams of the solid in 100 c.c. of solution. No solvent was employed for the methyl sulphate, slightly more of which was added than is represented by the ratio Me_2SO_4:NaOH. In each stage the temperature rose to 70° during the reaction, and the mixture was afterwards warmed gently until acid throughout.

1st Stage.—165 Grams of cotton wool, 500 c.c. of sodium hydroxide solution, 390 grams of methyl sulphate. Yield, 135 grams. Methoxyl content not determined.

2nd Stage.—135 Grams of the product from the first stage, 400 c.c. of sodium hydroxide solution, 236 grams of methyl sulphate. Yield, 98 grams. OMe = 20·4 per cent.

Action of Schweitzer's Reagent.—The product from the second stage, after remaining for seven days with 4 litres of Schweitzer's reagent, left 42 grams of undissolved residue containing OMe = 22·7 per cent. Three quantities of 3 grams each of the substance containing OMe = 22·7 per cent. were again treated each with 170 c.c. of Schweitzer's reagent:

(*a*) Residue after two days (1·5 grams) contained OMe = 23·1 per cent.

(*b*) Residue after five days (1·3 grams) contained OMe = 24·3 per cent.

(*c*) Residue after seven days (1·3 grams) contained OMe = 24·7 per cent.

The mixed residues were completely soluble in Schweitzer's reagent.

(*d*) By the action of Schweitzer's reagent on 28 grams of the substance containing OMe = 22·7 per cent., 4·4 grams of undissolved residue were obtained which contained OMe = 23·4 per cent. The 4·4 grams were again treated with Schweitzer's reagent so as to leave a small residue (weight not determined) which contained OMe = 28 per cent.

The Schweitzer's reagent was prepared by shaking freshly precipitated copper hydroxide with concentrated aqueous ammonia (D 0·88), and had D about 0·93. It was not standardised as regards content of ammonia or copper, but the reagent was tested to make sure that it dissolved cotton. The undissolved cellulosic residue was recovered by diluting the solution with aqueous ammonia, filtration through nickel gauze, and washing with aqueous ammonia and water. Small quantities were recovered by allowing the filtered solution to settle.

The methyl cellulose, the hydrolytic products from which have been described (T., 1914, **105**, 2357), was prepared in six stages; in the first five, the solution of sodium hydroxide contained 17 grams of the solid in 100 c.c., and the product contained OMe = 20·7 per cent. In the final stage the sodium hydroxide solution contained 38·3 grams of the solid in 100 c.c., and the product contained OMe = 23·6 per cent.

II. *Methyl Cellulose containing* OMe = 39·5 *per cent.*—This substance was prepared in nine stages. After three stages, in each of which the material was impregnated with half its weight of sodium hydroxide added as a solution containing 21·4 grams of the solid in 100 c.c., the OMe content was 24·8 per cent. In all the stages, somewhat less methyl sulphate was employed than is represented by the ratio Me_2SO_4 : NaOH, and the substance remained alkaline after the reaction was over. From 160 grams of cotton wool were obtained 135 grams, the yield being 79 per cent. of that obtainable of a product having OMe = 24·8 per cent.

In the later stages, the sodium hydroxide solution contained 38·8 grams of the solid in 100 c.c. Difficulties were encountered in impregnating the material with the alkaline solution, and the material was cut up into small pieces, squeezed in a press, pounded, etc., so that there was considerable loss. The percentage of methoxyl remained stationary from the eighth to the ninth stage (OMe = 39·7—39·5 per cent.).

Action of Schweitzer's Reagent.—2·8 Grams of the product containing OMe = 39·5 per cent., after treatment with 50 c.c. of Schweitzer's reagent for four days, gave 2·6 grams of undissolved residue containing OMe = 40 per cent.; 2·4 grams of this residue, on further treatment with Schweitzer's reagent, were reduced to 2·2 grams, which contained OMe = 40·4 per cent.

the *Copper Reduction.*—0·978 Gram of substance (OMe = 39·5 per
is, it) was treated with Fehling's solution, as in the examination
washed on. 0·15 C.c. of $N/10$-sodium thiosulphate was required for
on of the reduced copper. Cu_2O = 0·11 per cent.
was mecha *aration of Methyl Cellulose, using Ether.*—One
not been fo.
ation attained

hundred grams of cotton wool were soaked for one day in 1 litre of a solution of sodium hydroxide (20 grams in 100 grams of solution), and then drained and pressed, so that 350 grams of the solution (containing 70 grams of sodium hydroxide) were left. One hundred c.c. of methyl sulphate and 700 c.c. of ether were added, the mixture was heated under reflux for a few hours, and the ether was then removed by distillation. The weight of the washed and dried product was 105 grams. A repetition of this process gave 107 grams of a product containing OMe=24·5 per cent. In a third and fourth repetition of the process, where the impregnation of the material by the solution of alkali was assisted by exhausting the containing vessel, less sodium hydroxide was retained. The product from the fourth treatment contained OMe=31·3 per cent. and weighed 104 grams, the yield being thus 91 per cent. of the theoretical. The weights were determined under similar conditions after drying the material in a steam-oven.

Action of Schweitzer's Reagent.—From 2·88 grams of substance (OMe=31·3 per cent.), after immersion in 100 c.c. of Schweitzer's reagent for three hours, 1·93 grams of undissolved substance (OMe=32·4 per cent.) were recovered.

Eighty-eight grams of methyl cellulose containing OMe=15·6 per cent., which had been made in one stage, using ether, were immersed in 600 c.c. of Schweitzer's reagent for three days, when 8·4 grams of undissolved material were recovered containing OMe=15·2 per cent.

IV. *Methyl Cellulose containing more than* 40 *per cent. of Methoxyl.*—Highly methylated products were prepared by variants of the methods already described. For one of these, the following analytical results were obtained (Found: C=52·19; H=7·63; OMe=44·6 per cent. Trimethyl cellulose, $C_9H_{16}O_5$, requires C=52·9; H=7·84; OMe=45·6 per cent.).

Action of Solvents.—The behaviour of a preparation containing OMe=42 per cent. was examined towards alcohol, acetone, and Schweitzer's reagent. 1·8802 Grams, after being extracted with alcohol for three hours in a modified Soxhlet apparatus, weighed 1·8796 grams. The same sample was then extracted in the same way with acetone for three hours, and afterwards weighed 1·8790 grams. 0·408 Gram of the same substance was immersed in Schweitzer's reagent for twenty-four hours; the weight of the undissolved substance recovered was 0·407 gram.

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VIII.—*The Reaction between Nitric Acid and Copper.*

By Lancelot Salisbury Bagster.

On attempting to measure the volume of nitric oxide produced by the action of $5N$-nitric acid on copper under certain conditions, it was found that when the gaseous products were evolved and passed into sodium hydroxide solution in a vacuum, complete *absorption took place, although a considerable volume of nitric* oxide should have been obtained (Higley, *Amer. Chem. J.*, 1905, **17**, 18). This reaction was investigated in the hope of throwing further light on the reaction between nitric acid and copper. Veley (*Phil. Trans.*, 1891, **182**, 279) showed that the nitrous acid present was the cause of solution in dilute acid, and proposed a series of reactious involving the reduction of the nitrous acid to nitric oxide, followed by the oxidation of the nitric oxide to nitrous acid by the nitric acid. The work of Lewis and Edgar (*J. Amer. Chem. Soc.*, 1911, **33**, 292) shows that there is an equilibrium between nitric acid, nitric oxide, and nitrous acid, and that this equilibrium is but slowly attained. It seems unlikely, therefore, that in such case the nitric oxide would be completely and instantly oxidised, as would be necessary to secure complete absorption of the product in the experiment just described.

The following explanation of the process, in terms of well-known electrochemical theory, is suggested: (1) oxidation of the hydrogen film on the copper by the nitrous acid, which itself is reduced to hyponitrous acid, the copper passing into solution to replace the hydrogen removed; (2) oxidation of the hyponitrous acid to nitrous acid by nitric acid, which itself is reduced to nitrous acid. It may be assumed that the first reaction will produce hyponitrous acid in unimolecular form ($H_2 + HNO_2 \longrightarrow H_2O + HNO'$), and as Divers (T., 1889, **75**, 112) has shown that hyponitrous acid has the double molecule, it may be considered that at the moment of formation it will be in a reactive state corresponding with nascent hydrogen, and completely oxidised by nitric acid. It will be shown that the product of reaction with t-dilute acid is nitrous acid, produced in quantity necessary to is, tisfy the above scheme. It might be expected that sufficiently washte nitric acid would fail to oxidise completely the hyponitrous was meermed, and in such case nitrous oxide, the well-known decom-not been product of hyponitrous acid, should appear as a product. ation attain

This has been found to be the case by Higley (*loc. cit.*), using $3N$ and more dilute acid. It would not be expected that much nitrous oxide should be obtained; if the nitric acid were so weak that it failed to oxidise most of the hyponitrous acid, the reaction would cease when the nitrous acid originally present was exhausted. This has been found to be the case with $N/2$-nitric acid. Reaction started by addition of sodium nitrite ceased when the nitrous acid was destroyed, but could be restarted by the addition of more nitrite.

Divers (*loc. cit.*) has shown that nitrous acid oxidises hyponitrous acid, with the formation of nitric oxide and water, and in the course of the present work it was found that nitric oxide is the only gaseous product of reaction between copper and an excess of $N/3$-nitrous acid, prepared by adding sodium nitrite solution to excess of dilute hydrochloric acid. Here, hyponitrous acid formed would, in the absence of nitric acid, be oxidised by the excess of nitrous acid. As in the case of very dilute nitric acid, it would be expected that very dilute nitrous acid would also produce some nitrous oxide. This has been verified in the case of $N/50$-nitrous acid, prepared as above, reacting with an excess of copper. Nitric oxide was produced, but at the end of the reaction the gas in solution was collected, and found to consist largely of nitrous oxide. The nitrous oxide was probably formed when the nitrous acid had become nearly exhausted. It is unlikely that the hyponitrous acid will be oxidised by nitrous acid in the presence of much nitric acid, as the nitrous acid in the neighbourhood of the copper will react with it, and conditions will consequently be favourable for oxidation of the product by the nitric acid, if present in quantity.

Further, Peters (*Zeitsch. anorg. Chem.*, 1919, **107**, 313) states that in the presence of carbon dioxide, a 5 per cent. solution of sodium nitrite reacts with copper, producing nitric and nitrous oxides, nitrate being formed in solution. Known constants for nitrous and carbonic acids show that about 0·25 per cent. of the nitrite will be present as free acid, which at this very small concentration will react with the copper in the manner already discussed, the same products being obtained. The nitrate would be formed by direct decomposition of the nitrous acid.

Reference should finally be made to the work of Ackworth and Armstrong (T., 1877, **32**, 54), where it is shown that copper salts in solntion give rise to an increased yield of nitrous oxide. These authors used a small volume of nitric acid, and it is probable that as the acid became used up, the nitrous acid accumulated in solution would react with the hyponitrous acid formed. A deep blue

colour characteristic of complex copper salts was noticed when copper was dissolved in nitrous acid during the present work. This complex, in the case of Armstrong's work, would diminish the concentration of free nitrous acid, thus leading to the formation of a greater quantity of nitrous oxide.

So far, discussion has been confined to dilute acid. It has been shown (Ihle, *Zeitsch. physikal. Chem.*, 1895, **19**, 577) that nitric acid above 35 per cent. by volume will react in the absence of nitrous acid. This concentration corresponds with just under 8*N*. Reference to the table (p. 86) shows that such acid yields nitrogen peroxide as well as trioxide. As a secondary reaction is not apparent in the experiments described with dilute acid, it is probable that the products obtained from stronger acid nearly represent primary ones. The nitrogen peroxide may be regarded as the product of the direct oxidation process by the nitric acid, the nitrous anhydride also obtained in quantity from 8*N*- and 10*N*-acid being due to the simultaneous progress of both types of reaction.

EXPERIMENTAL.

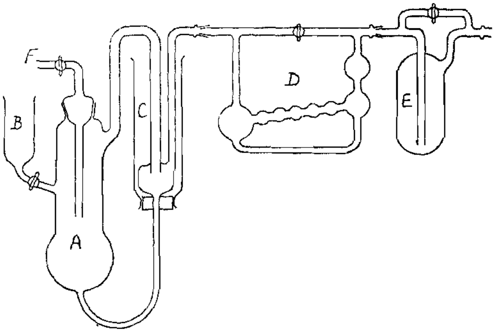
When the experiment described at the beginning of this work was carried out quantitatively, it was found that the absorbing solutions contained nitrite corresponding with from 310 to 320 c.c. of *N*/10-permanganate for every gram of copper dissolved. This result was obtained with the product of reaction from acid of strength from 5*N* to 15*N*. The theoretical quantity of permanganate corresponding with the reactions discussed is 318 c.c., being the same whether the product is nitrous anhydride, nitrogen trioxide, or nitrogen peroxide. Nitrous acid, if formed, would be expected, under the conditions described, to distil as anhydride, owing to the equilibrium

$$2HNO_2 \rightleftharpoons H_2O + N_2O_3.$$

To distinguish between the possible products, it was necessary to determine the total nitrogen in the absorption vessel, apart from any that might distil there directly as nitric acid. For this purpose, the apparatus shown in the figure was constructed. Nitric acid was admitted after exhaustion to the vessel, *A*, containing the copper by means of the funnel, *B*. Nitric acid was condensed in *C* and returned to *A*. Gaseous products were absorbed in *D* and *E*, which contained sodium hydroxide solution. Connexion with the mercury pump was closed by a tap during reaction. Tests with this apparatus in the absence of copper showed that no

appreciable quantity of nitric acid distilled through the condenser when cooled to 10°.

In the course of preliminary tests, using $10N$ and weaker acid, it was found that when the condenser was cooled to 0°, nitric oxide was produced there, the effect being still slightly apparent at 10° with $6N$-acid. The probable explanation is that, gaseous trioxide being a mixture, at the lower temperature the nitrogen peroxide is partly condensed, thus allowing the nitric oxide to pass on and through the alkali unabsorbed. This effect would at once be apparent in the case of trioxide; if excess of peroxide were also present, greater condensation would have to take place before the composition fell below that corresponding with trioxide, when



complete absorption would cease and nitric oxide appear. The production of nitric oxide will be accompanied by a diminished quantity of products in the absorption train.

In carrying out an experiment, the nitric acid was kept boiling, the temperatures shown in the table being the boiling points of the acid solutions in a vacuum. A slow stream of carbon dioxide was passed through the tube F to sweep the gaseous products from the condenser after removal of the acid vapour. For analysis, the nitrite in a portion of the absorption solution was determined with permanganate, and the total nitrogen in the residue estimated as ammonia by distillation with Devarda's alloy. A series of results is shown in the following table. In each case, 0·250 gram

of copper was used, and at least ten times the quantity of acid needed for solution.

No.	Nitric acid. D.	Normality of acid.	Temperature.	Nitrogen as N_2O_3. Gram.	Total nitrogen. Gram.	N_2O_4. Per cent.	Nitrogen as NO. Gram.	Temperature of condenser.
1	1·40	14·5	60°	0·0553	0·0980	77	—	10°
2	1·40	14·5	60	0·0546	0·1001	80	—	10
3	1·30	10	45—50	0·0557	0·0616	10·2	—	10
4	1·30	10	45—50	0·0560	0·0630	11·0	—	10
5	1·30	10	45—50	0·0542	0·0600	10·5	—	5
6	1·25	8	35—40	0·0542	0·0582	7·2	—	10
7	1·20	6	30	0·0550	0·0610	(10·8)	—	16
8	1·20	6	30	0·0490	0·0490	—	0·0045	10
9	1·20	6	30	0·0420	0·0423	—	0·0090	7
10	1·17	5	30	0·0546	0·0595	(9)	—	20

The theoretical quantity of trioxide to satisfy the reactions suggested is 0·0555 gram, the total nitrogen being the same when trioxide is the product, and twice the amount if peroxide is the only product.

The blank tests showed that in the case of experiments 1 to 6 there was no nitric acid distilled to make the total nitrogen value high. The small loss of nitrogen mentioned as occurring with the weak acid must still be considered as taking place, however, with the condenser at 10°. Although, as explained, this loss will not be apparent in the trioxide value, it will introduce an error of a few milligrams in the total nitrogen value. In the case of experiments 7 and 10, the value for the total nitrogen is higher than it should be; the copper in the case of the 6*N*-acid required a considerable time for solution, the acid occasionally "boiled with bumping," and unless the temperature of the condenser was as low as 10°, nitric acid reached the absorbers by direct distillation. Values such as are shown were repeatedly obtained, but it was not possible to secure a more definite result. As already indicated, the fact that the product from 5*N*- and 6*N*-acid more easily forms nitric oxide than that from 8*N*- and 10*N*-acid shows that it contains less peroxide. Considering the facts stated, it may be concluded that the product from 5*N*- and 6*N*-acid is almost entirely nitrogen trioxide (nitrous anhydride). The low values for the products in experiments 8 and 9 will be raised to the same value as the others if allowance is made for the nitrogen lost, owing to the formation of nitric oxide, this value being nearly that demanded by theory.

Allowing for the correction suggested for the products from more concentrated acid, the product from 14·5*N*-acid will contain 85 to 90 per cent. of peroxide, the residue being trioxide, for 10*N*-

acid there will be about 15 to 20 per cent. of peroxide, and for the $8N$-acid somewhat less.

It was not practicable to carry out work with acid more dilute than $5N$, owing to the time taken for solution in a vacuum, probably on account of the continuous removal of nitrous acid, which in consequence could not exert its usual "auto-catalytic" effect.

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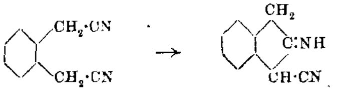
IX.—*The Formation of Derivatives of Tetrahydronaphthalene from γ-Phenyl Fatty Acids.*

By GEORGE ARMAND ROBERT KON and ARNOLD STEVENSON.

THE conditions governing the formation of dicyclic structures of the naphthalene type from benzene derivatives having a side-chain of not less than four carbon atoms are, at present, difficult to determine, because we have, as yet, little knowledge of the effect on the valency directions of carbon atoms caused by their participation in an aromatic nucleus. That, however, the conditions are very similar to those which determine the formation of similar monocyclic structures from open-chain carbon derivatives has been clearly shown by experiments which have been carried out on the formation of ring structures through the catalytic action of sodium ethoxide on the relevant dinitrile. Thus it has been shown by Moore and Thorpe (T., 1908, **93**, 176) that the transformation



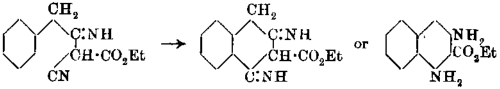
takes place with the greatest ease, and by Thorpe (T., 1909, **95**, 1901) that the change

$$\begin{matrix} CH_2\cdot CH_2\cdot CN \\ CH_2\cdot CH_2\cdot CN \end{matrix} \longrightarrow \begin{matrix} CH_2 - CH \\ CH_2\cdot CH(CN) \end{matrix} > C{:}NH$$

can, apparently, be effected with equal readiness.

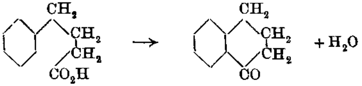
That six-membered rings of the two types also exhibit similar behaviour is to be inferred from the results of a number of experi-

ments, of which the transformation represented below may be taken as an example (Atkinson and Thorpe, T., 1906, **89**, 1920):



Scheme (*a*).

It is therefore remarkable that hitherto no examples appear to have been recorded illustrating the formation of a six-carbon saturated ring by the elimination of water from a γ-phenyl fatty acid through the combination of the hydroxyl group of the carboxylic complex with a hydrogen atom in the ortho-position of the benzene nucleus. The simplest compound which could exhibit this change would be γ-phenylbutyric acid (I), but although this

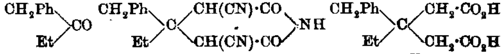


(I.)

acid has been made the subject of exhaustive study by several investigators, no record appears to have been made of any such reaction. The matter is an important one, because, if a change of this kind cannot be effected, it would indicate that there is an essential difference between the conditions determining ring formation in open-chain compounds and those of the type under discussion, and that the latter are not readily formed unless there is the possibility of the production of the true naphthalene nucleus, as illustrated by scheme (*a*).

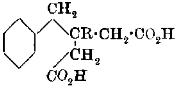
That this is not the case is shown in the present paper, wherein is described the formation of derivatives of tetrahydronaphthalene from two typical derivatives of γ-phenylbutyric acid. It is also shown that a derivative of γ-tetrahydrophenylbutyric acid can be caused to undergo the same change.

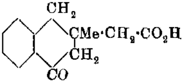
It was evident that, on theoretical grounds, the derivatives of γ-phenylbutyric acid for use in these experiments should have been formed by hydrolysing the condensation products obtained by condensing a suitable ketone with ethyl cyanoacetate and ammonia in accordance with Guareschi's method, but it has been



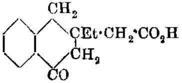
(II.) (III.) (IV.)

shown already by Kon and Thorpe (T., 1919, **115**, 704) that the acid produced by hydrolysing the condensation product (III) formed from benzyl ethyl ketone (II) by means of sulphuric acid does not possess the expected formula (IV), but has an abnormal structure. Attention was therefore directed towards determining the structure of this abnormal product, as well as that derived in a similar manner from benzyl methyl ketone, and it was soon found that they were actually the tetrahydronaphthalene derivatives, (V) and (VI), which had been formed by the elimination of water during the process of hydrolysis. The correctness of this





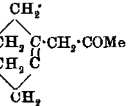
(V.)



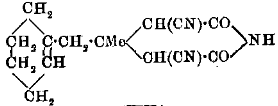
(VI.)

view of the constitution of these acids was shown by the formation of semicarbazones and by the production of phthalic acid on oxidation with permanganate.

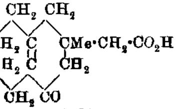
In order to show that the condition of the benzene nucleus did not have any appreciable effect on the formation of the second ring, experiments were then carried out with the tetrahydroketone (*cyclo*hexenylacetone, VII), and in this case also the hydrated naphthalene derivative (IX) is the sole product formed on hydrolysing the imide (VIII) with sulphuric acid. It seems,



(VII.)



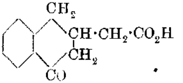
(VIII.)



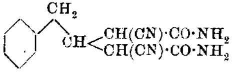
(IX.)

therefore, as if the ease with which a ring closes is influenced by the character of the groups attached to the β-position of the side-chain. It will be remembered that this point was raised in a recent paper (Day and Thorpe, T., 1920, **117**, 1465), but it is evident that much more experimental evidence will be necessary before any definite pronouncement can be made.

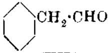
An attempt was made to prepare the simplest member of the phenyl series (X) by hydrolysing the condensation product (XI) produced from phenylacetaldehyde (XII) and cyanoacetamide in accordance with the method of Day and Thorpe (*loc. cit.*), but up to the present we have only succeeded in obtaining a small quantity of the compound (XI), because, under the usual conditions, the chief product is evidently derived from the interaction of cyano-



(X.)



(XI.)



(XII.)

acetamide and phenylacetaldehyde in equimolecular proportions. Its structure has not, as yet, been completely elucidated, and as it presents several points of interest, it is proposed to investigate it more fully.

The behaviour of the acid (V) on regulated oxidation is interesting, a number of intermediate compounds being formed before phthalic acid is finally produced. It is hoped to make these compounds the subject of a subsequent communication.

EXPERIMENTAL.

ac.-1-*Keto-3-methyltetrahydronaphthyl-3-acetic Acid* (V, p. 89).

It was found that for the hydrolysis of the imide derived by Guareschi's process (*Atti R. Accad. Sci. Torino*, 1900—1901, **36**, 443) from benzyl methyl ketone, Thole and Thorpe's method (T., 1911, **99**, 445) did not give very satisfactory results, the best yield being obtained with a large excess of 50 per cent. sulphuric acid (by volume). Twenty grams of imide were heated under reflux with 400 c.c. of acid, with frequent shaking, until solution took place and evolution of gas ceased, when the liquid had become dark

red. After diluting with 150 c.c. of water, it was extracted with ether, yielding 12—14 grams of crude product (theory, 16·3).

The crude acid is yellow or brown, but on twice recrystallising from benzene, it is obtained in stellate clusters of colourless prisms melting at 155—156° (Found: C = 71·35; H = 6·53. $C_{13}H_{14}O_3$ requires C = 71·5; H = 6·5 per cent. Silver salt. Found: Ag = 32·97. $C_{13}H_{13}O_3Ag$ requires Ag = 33·2 per cent.). It is a weak acid, not effervescing with sodium hydrogen carbonate, and, after boiling with 10 per cent. sodium hydroxide solution, it is precipitated by acid unchanged. The silver, mercuric, lead, cupric, chromium, aluminium, ferric, and ferrous salts form readily in the cold from the ammonium salt, whilst the barium and calcium salts are soluble both in the cold and on boiling.

The *semicarbazone* was prepared by warming an alcoholic solution of the acid with semicarbazide acetate. On keeping, a dense, crystalline mass formed, which, on recrystallising from alcohol, separated in fine needles melting at 221° (Found: N = 15·44. $C_{14}H_{17}O_3N_3$ requires N = 15·3 per cent.).

The oxidation to phthalic acid with potassium permanganate can be effected both in acid and alkaline solution. In the case of the former, 4 grams of the acid (V) were dissolved in 150 c.c. of sulphuric acid (1 part of acid to 2 parts of water), and a warm, saturated solution of potassium permanganate was added, with heating, until the supernatant liquid, above the precipitate which formed, was pink. The excess of permanganate was destroyed with oxalic acid, and the liquid extracted with ether, when 1 gram of crude phthalic acid was obtained. After recrystallisation from alcohol and again from water, it melted and decomposed at 203°, and on heating with resorcinol gave fluorescein (Found: C = 57·65; H = 3·83. Calc.: C = 57·8; H = 3·6 per cent.).

The alkaline oxidation was carried out by dissolving the acid in sodium hydroxide solntion, heating on the steam-bath, and adding a warm, saturated solution of potassium permanganate until the colour persisted. After destroying the excess of permanganate with sulphurous acid and filtering, the liquid was extracted with ether, the ethereal extract yielding crude phthalic acid, which was identified as before.

ac.-1-*Keto-3-ethyltetrahydronaphthyl-3-acetic Acid* (VI, p. 89).

In preparing this acid, it is advisable to use the pure imide, as otherwise an oil is formed, which prevents the separation of the acid. Eight grams of imide were heated under reflux with 160 c.c.

of sulphuric acid (1 part of acid to 1 part of water by volume), with frequent shaking, until solution took place and evolution of gas ceased. After diluting with water, it was extracted with ether, the ethereal extract giving on evaporation an oil, which solidified in a vacuum, yielding 1·4 grams of crude product. On recrystallisation from benzene and light petroleum, it separated in short, stout prisms, which adhered firmly to glass and melted at 79° (Found: C=72·18; H=6·65. $C_{14}H_{16}O_3$ requires C=72·4; H=6·9 per cent. Silver salt. Found: Ag=31·91. $C_{14}H_{15}O_3Ag$ requires Ag=31·8 per cent.). The metallic salts resemble those of its homologue, the barium and calcium salts being soluble both in the cold and on heating, whilst the salts of the heavy metals are readily precipitated in the cold.

The *semicarbazone*, prepared by treating an alcoholic solution of the acid with semicarbazide acetate, was twice recrystallised from alcohol, when it separated in needles melting at 210° (Found: N=14·73. $C_{15}H_{19}O_3N_3$ requires N=14·5 per cent.).

The oxidation to phthalic acid was carried out in acid solution in the manner already described (p. 91), and was identified by the resorcinol test.

Condensation of cyclo*Hexenylacetone with Ethyl Cyanoacetate: 3 : 5-Dicyano-2 : 6-diketo-4-*cyclo*hexenylmethyl-4-methylpiperidine* (VIII, p. 89).

The ketone was prepared by Wallach's method from *cyclo*hexanone and acetone (*Annalen*, 1912, **394**, 362), 13·8 grams being condensed with ethyl cyanoacetate and alcoholic ammonia by Guareschi's method (*loc. cit.*), giving 12 grams of crude imide. When twice crystallised from alcohol, it separated in colourless needles, which shrank and darkened at 190° and melted and decomposed at 202° (Found: N=15·72. $C_{15}H_{17}O_2N_3$ requires N=15·5 per cent.).

1-*Keto-3-methyloctahydronaphthyl-3-acetic Acid* (IX, p. 89).

It was again found that the use of impure imide gave unsatisfactory results. Concentrated sulphuric acid violently attacks the imide in the cold, but with an excess of 50 per cent. acid (by volume) the reaction proceeds smoothly. On heating under reflux until evolution of gas ceased, and then diluting and extracting with ether, an oil was obtained from the ethereal extract, which solidified on leaving in a vacuum, but the yield was rather poor, being only about 25 per cent. of the theoretical. On recrystallisa-

tion from ether, the acid separated in colourless crystals, which were, however, indefinite in form, melting at 90° (Found: C=70·05; H=8·17. $C_{13}H_{18}O_3$ requires C=70·2; H=8·2 per cent. Titration with N/10-sodium hydroxide. Found: 8·25 c.c. Calc. (monobasic): 8·05 c.c. Silver salt. Found: Ag = 32·81. $C_{13}H_{17}O_3Ag$ requires Ag=32·8 per cent.).

The metallic salts closely resemble those of the two acids described above, the barium and calcium salts being soluble both in the cold and on heating, whilst those of the heavy metals form readily in the cold.

The *semicarbazone* was prepared by treating an alcoholic solution of the crude acid with semicarbazide acetate. It is very sparingly soluble in hot alcohol, and, after twice crystallising therefrom, formed spherical aggregates of needles melting and decomposing at 209—210° (Found: N=15·06. $C_{14}H_{21}O_3N_3$ requires N=15·1 per cent.).

The oxidation to phthalic acid was carried out with potassium permanganate and sulphuric acid in the manner described above, crude acid being employed. Phthalic acid was identified by the resorcinol test.

Condensation of Phenylacetaldehyde with Cyanoacetamide.

Cyanoacetamide (8·4 grams) and phenylacetaldehyde (6 grams) were dissolved in 50 c.c. of water and sufficient alcohol to effect complete solution, and 0·5 c.c. of a 50 per cent. aqueous solution of potassium hydroxide was added.

The crystalline precipitate, which had formed in the course of twenty-four hours, was collected, and found to consist of two substances, which can be separated by extracting the mixture with boiling alcohol. The insoluble residue, which forms small needles melting at 245°, is the *diamide* of *αα′-dicyano-β-benzylglutaric acid*, $CH_2Ph·CH[CH(CN)·CO·NH_2]_2$ (Found*: C=62·00; H=5·35; N=20·57. $C_{14}H_{14}O_2N_2$ requires C=62·2; H=5·2; N=20·7 per cent.). The quantity of this substance obtained up to the present is too small for the investigation of its behaviour on hydrolysis.

The second substance, which separates on cooling the alcoholic extract, crystallises in needles melting at 204°. We have not yet succeeded in obtaining concordant figures on analysis, but the nitrogen content (13·8—14·0 per cent.) clearly indicates that the substance is formed by the condensation of cyanoacetamide and phenylacetaldehyde in equimolecular proportions.

* We are indebted to Mr. J. N. E. Day for this analysis.

We are indebted to Professor J. F. Thorpe for much valuable advice and for the interest he has taken in our work; our thanks are also due to Mr. W. S. G. P. Norris, of this College, for kindly preparing some of the materials required.

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[*Received, December 17th, 1920.*]

X.—*The Action of the Chlorides of Sulphur on Substituted Ethylenes. The Action of Propylene on Sulphur Monochloride and the Synthesis of ββ'-Dichlorodi-*n*-propyl Sulphide.*

By SAMUEL COFFEY.

GUTHRIE (*Quart. Journ. Chem. Soc.*, 1859, **12**, 116), by the action of ethylene on sulphur dichloride, obtained impure ββ'-dichlorodiethyl sulphide. Later (*ibid.*, 1860, **13**, 134) he obtained the disulphide by the action of ethylene on sulphur monochloride at 100°, but higher chlorinated products and tar were also formed in large quantity. In a recent communication Gibson and Pope (T., 1920, **117**, 271) have shown that sulphur monochloride and ethylene between the ordinary temperature and 70° give ββ'-dichlorodiethyl sulphide, whereas above 70° the liquid darkens and hydrogen chloride is evolved as in Guthrie's reaction.

Apart from the work mentioned above, nothing is known of the reactions involved when sulphur chlorides act on olefines, although the action of "sulphur chloride" on oils, etc., has long been used as a "thermal" test for unsaturation.

The aim of these investigations, of which this is only a preliminary communication, is to study the action of sulphur chlorides on substituted ethylenes, to find the effect of the substituent on the course of the reaction, with a view to elucidate the complex changes which doubtless are involved in the thermal test mentioned above.

Considering the mono-substituted ethylenes, the compounds most likely to be produced are of the types:

$CHRCl{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}CHRCl$ (I.)

$CH_2Cl{\cdot}CHR{\cdot}S{\cdot}S{\cdot}CHR{\cdot}CH_2Cl$ (II.)

$(CHRCl{\cdot}CH_2)_2S$ (III.)

$(CH_2Cl{\cdot}CHR)_2S$ (IV.)

The course of the reaction will no doubt depend on the temperature and the electrochemical character of the substituent group.

In the case of a monoalkyl-ethylene, such as propylene, for example, the electropositive methyl group should cause the secondary chloride to be produced as the main product, as in the case of iodine chloride (Michael, *J. pr. Chem.*, 1892, [ii], **46**, 345), and therefore the probable products will be $\beta\beta'$-dichlorodi-*n*-propyl disulphide (type I) and $\beta\beta'$-dichlorodi-*n*-propyl sulphide (type III).

Attempts to prepare these substances by the action of propylene on sulphur monochloride were not very successful, but a small quantity of *$\beta\beta'$-dichlorodi*-n-*propyl disulphide* was obtained, from which a *barium chloropropanesulphonate* was produced on oxidation. *$\beta\beta'$-Dichlorodi*-n-*propyl sulphide*, which was not formed in this reaction, was prepared from propylene chlorohydrin by Clarke's modification of V. Meyer's method (T., 1912, **101**, 1583) for the production of $\beta\beta'$-dichlorodiethyl sulphide:

$$CH_3\cdot CH(OH)\cdot CH_2Cl \longrightarrow \underset{(V.)}{(CH_3\cdot CH[OH]\cdot CH_2)_2S} \longrightarrow \underset{(VI.)}{(CH_3\cdot CHCl\cdot CH_2)_2S}.$$

EXPERIMENTAL.

Action of Propylene on Sulphur Monochloride.

The sulphur monochloride was repeatedly distilled from sulphur and finally fractionated in a vacuum over charcoal; 2·5 per cent. of sulphur was dissolved in the amber-coloured liquid.

The propylene was prepared by the action of phosphoric acid on *iso*propyl alcohol (Newth, T., 1901, **79**, 915). The dried propylene was passed into the sulphur monochloride (40 grams) at a rate of about a litre per hour, the absorption vessels being kept at constant temperature.

At 60° the sulphur monochloride soon became brown and gelatinous, and finally changed into a viscid, black product through which the gas would not pass. During the whole time much hydrogen chloride was evolved. When distilled in a current of steam the product furnished only about 1 gram of volatile oil.

In the next experiment the absorption was started at 40° and the temperature was never allowed to rise above 50°. Ten litres of gas (approximately 20 grams) were passed through three tubes, each of which contained 15 grams of sulphur monochloride, before all the chloride had become dark brown and semi-solid. The product was extracted with chloroform and then distilled (18—25 mm.), when a small quantity (5 grams) of a red oil (*A*) passed over at 113—120°.

The residue was a black tar (more than 25 grams). During the distillation much hydrogen chloride was evolved. The distillate, at first pale yellow, gradually became red as it passed over.

It was vigorously oxidised by concentrated nitric acid (D 1·4) in the cold, but nothing but a little sulphur separated on dilution. Thus the reaction was totally different from that of nitric acid on $\beta\beta'$-dichlorodi-*n*-propyl sulphide (p. 97).

The filtered solution was evaporated until free from nitric acid, when a pale yellow, viscous, strongly acid liquid was left. This was diluted with water, boiled with barium carbonate, and the filtrate evaporated to incipient crystallisation, when a barium salt separated on cooling. A little barium sulphate was also obtained.

The barium salt was only sparingly soluble in alcohol, but readily so in cold water or hot, 75 per cent. alcohol, from which it crystallised in colourless, nacreous plates. It contained sulphur and chlorine, and on treatment with phosphorus pentachloride gave a very easily hydrolysable sulphonyl chloride (Found, in air-dried salt, $H_2O = 5·25$. $(C_3H_6O_3ClS)_2Ba,1\frac{1}{2}H_2O$ requires $H_2O = 5·6$ per cent. Found, in anhydrous salt, $Ba = 30·7$. $(C_3H_6O_3ClS)_2Ba$ requires $Ba = 30·4$ per cent.).

This was therefore the *barium* salt of a *chloropropanesulphonic acid*, and the original substance was in all probability $\beta\beta'$-*dichlorodi*-n-*propyl disulphide*.

$\beta\beta'$-*Dihydroxydi*-n-*propyl Sulphide* (V).

Propylene chlorohydrin was prepared from allyl chloride by Oppenheim's method (*Annalen Suppl.*, 1868, **6**, 367), for as Smith (*Zeitsch. physikal. Chem.*, 1918, **93**, 59) has shown recently, this is the only method which does not give a mixture of α- and β-chlorohydrins.

Twelve grams of propylene chlorohydrin were gradually added to 37 grams of crystallised sodium sulphide dissolved in an equal weight of water. The mixture became warm, and was cooled in water, but after a short time the development of heat ceased. The mixture was heated on a water-bath for one and a-half hours; a pale brown oil gradually separated, but partly redissolved on cooling. The product was then just acidified with hydrochloric acid. The slightly turbid solution was distilled in a vacuum, when a yellow oil gradually separated along with sodium chloride. The residue was shaken with alcohol and the extract evaporated in a vacuum until no more distilled. The $\beta\beta'$-*dihydroxydi*-n-*propyl sulphide* was left as a non-volatile, pale yellow, viscous liquid, soluble in water or alcohol, and heavier than water. The product was not

purified further, but used for the preparation of ββ'-dichlorodi-*n*-propyl sulphide. The yield was 80 per cent. of the theoretical.

ββ'-Dichlorodi-n-propyl Sulphide (VI).

The preceding compound (9 grams) was added to concentrated hydrochloric acid (70 c.c.), when a pale pink, turbid solution was produced. This was then heated on a water-bath for one and a-half hours, when it gradually became more and more turbid, and a heavy, dark brown oil gradually separated. It was extracted with chloroform and distilled in a vacuum, when a colourless oil, boiling at 122°/23 mm., passed over. When the temperature quickly rose to 126°/23 mm. the distillation was stopped. The yield of ββ'-dichlorodi-*n*-propyl sulphide was 7 grams, and the residue amounted to less than 1 gram.

ββ'-Dichlorodi-n-propyl sulphide is a colourless oil, boiling at 122°/23 mm., which does not freeze on cooling to −8° for half an hour. It has properties very similar to its lower homologue, "mustard gas," except that apparently it has no vesicant action (Found, Cl = 38·10. $C_6H_{12}Cl_2S$ requires Cl = 37·90 per cent.).

When heated with alcoholic potassium hydroxide solution the chlorine is displaced quantitatively with the production of the dihydroxy-compound.

Oxidation of ββ'-Dichlorodi-n-propyl Sulphide.

When added to an excess of nitric acid (D 1·4) oxidation took place smoothly and a clear solution was obtained. On leaving for twenty-four hours and diluting, a heavy, viscid oil separated, which from its solubility in concentrated acid and insolubility on dilution appeared to be the sulphoxide (compare Davies, T., 1920, **117**, 299). In the hope that some crystalline compound might be obtained, this oil was heated for some time at 100° with more concentrated nitric acid. A rather vigorous oxidation took place, and on dilution a little oil separated; on concentrating the clear solution a solid melting at 100—102° crystallised, which was, in all probability, the corresponding sulphone.

Another product of the reaction was sulphuric acid, showing that under these conditions ββ'-dichlorodi-*n*-propyl sulphide is completely decomposed.

ADDENDUM.

Since these results were obtained, a paper by Conant, Hartshorn, and Richardson (*J. Amer. Chem. Soc.*, 1920, **42**, 485) has appeared,

in which it is shown that the production of $\beta\beta'$-dichlorodiethyl sulphide involves two reactions. An intermediate product, $CH_2Cl\cdot CH_2\cdot SCl$, has been obtained from ethylene and sulphur dichloride, which evolves hydrogen chloride very easily and when warmed with sulphur gives a black tar. In the case of sulphur monochloride, a similar product is obtained, and unless the sulphur is crystallised from the colloidal solution after the reaction, a black tar, $(CH_2Cl\cdot CH_2)_2S_5$, is formed.

The results given in this paper are in agreement with those described above, and probably a similar series of reactions takes place in the case of propylene, to some extent, but $\beta\beta'$-dichlorodi-*n*-propyl sulphide has not yet been detected.

The author desires to express his indebtedness to Professor F. S. Kipping, F.R.S., for his interest in and criticisms of this work.

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[*Received, December 9th*, 1920.]

XI.—2 : 4 : 6-*Trinitrotolylmethylnitroamine.*

By OSCAR LISLE BRADY and WILLIAM HOWIESON GIBSON.

TRINITROTOLYLMETHYLNITROAMINE has been described by Blanksma (*Rec. trav. chim.*, 1902, **21**, 327), who prepared it by the nitration of 2:4:6-trinitromethyl-*m*-toluidine obtained by the action of methylamine on 2:4·6-trinitro-*m*-tolyl methyl ether. The preparation of this compound from 2:3:4- and 3:4:6-trinitrotoluenes has now been studied.

In 2:3:4- and 3:4:6-trinitrotoluenes one of the nitro-groups is mobile and is readily displaced by treatment with amines. In the case of the latter compound Hepp (*Annalen*, 1882, **215**, 344) showed that it was the 3-nitro-group that was displaced. In the case of 3:4:6-trinitrotoluene it has been shown that the dinitrotoluidine obtained by the action of ammonia is the same as that obtained as the main product in the nitration of aceto-*m*-toluidide (Cook and Brady, T., 1920, **117**, 751), and the synthesis of 2:4:6-trinitrotolylmethylnitroamine from 3:4:6-trinitrotoluene confirms the fact that the 3-nitro-group is also the mobile one in this compound. These trinitrotoluenes accordingly follow the rule given by Meldola (T., 1908, **93**, 1659) for the mobility of groups in negatively substituted benzene derivatives.

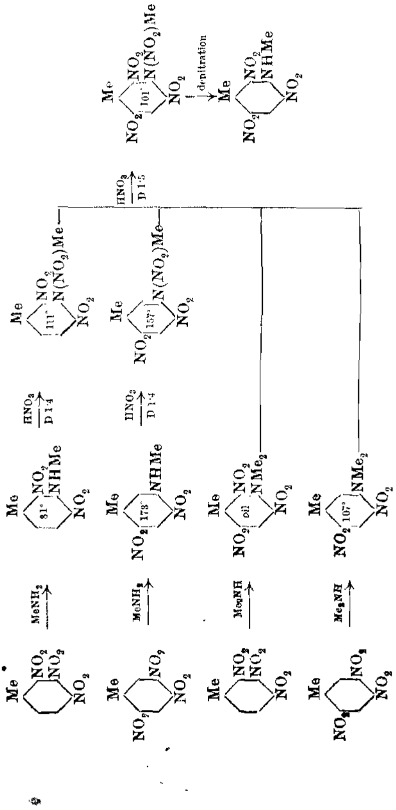
When 2 : 3 : 4- and 3 : 4 : 6-trinitrotoluenes are treated with methylamine or dimethylamine the corresponding dinitromethyl-*m*-toluidines and dinitrodimethyl-*m*-toluidines are formed, all of which form 2 : 4 : 6-trinitrotolylmethylnitroamine on nitration.

In the case of the dinitromethyl-*m*-toluidines the first action of the nitrating acid apparently consists in the formation of a dinitronitroamine, more energetic nitration resulting in a further nitro-group entering the ring. It has not been found possible to obtain 2 : 4 : 6-trinitromethyl-*m*-toluidine by direct nitration of either 2 : 4- or 4 : 6-dinitromethyl-*m*-toluidine, but it has been prepared by denitration of the nitroamine. In the case of the dinitrodimethyl-*m*-toluidines the intermediate trinitrodimethyltoluidine has not been obtained; these compounds are not acted on by nitric acid of density 1·4, and are completely nitrated with the elimination of a methyl group by nitric acid of density 1·5 or by a mixture of nitric and sulphuric acids. The reactions are summarised on p. 100.

EXPERIMENTAL.

2 : 3 : 4- *and* 3 : 4 : 6-*Trinitrotoluenes*.—The nitration of *m*-nitrotoluene is described by Hepp (*loc. cit.*). A mixture of 2 : 3 : 4- and 3 : 4 : 6-trinitrotoluenes is obtained, and Drew (T., 1920, **117**, 1615) has shown that about 7 per cent. of 2 : 3 : 6-trinitrotoluene is also produced. Hepp separated the 2 : 3 : 4- and 3 : 4 : 6-compounds by crystallisation from carbon disulphide. A more convenient method of preparation and separation than that described by Hepp is as follows.

A mixture of 160 c.c. of nitric acid (D 1·42) and 340 c.c. of sulphuric acid (96 per cent.) is added in small portions at a time to 225 grams of *m*-nitrotoluene, the temperature being kept in the neighbourhood of 50°. When all the acid has been added, the mixture is slowly heated to 100° on the water-bath and kept at this temperature for thirty minutes with frequent shaking. The mixture is then allowed to cool to 50° and separated. The oil is added slowly to a mixture of 180 c.c. of nitric acid (D 1·5) and 410 c.c. of sulphuric acid (96 per cent.). The mixture is warmed to 70° and kept at that temperature for thirty minutes with frequent shaking, and then cautiously heated to 100°, at which temperature it is kept for one hour. The oil is separated from the acid while still hot, run into cold water, and washed by the injection of steam until free from acid. On cooling and keeping, the oil sets to a pasty solid, which is collected and dissolved in boiling alcohol (about 100 c.c. of 95 per cent. spirit for 12 grams of the mixture). The solution is cooled to about 50° and seeded with a little pure 3 : 4 : 6-trinitro-


MeNH2
Me2NH
HNO3 D 1·4
HNO3 D 1·5
denitration
81°
173°
oil
107°
111°
157°
101°

toluene and shaken vigorously. After two to three minutes a fair quantity of solid will have separated in the form of sandy crystals, which are at once collected. The filtrate is precipitated with water, and the solid, after being freed as much as possible from water by pressing, dissolved in boiling glacial acetic acid (about 100 c.c. of acid for 50 grams of solid). The solution is cooled to about 60°, a very small quantity of water added, and a crystal or so of 2 : 3 : 4-trinitrotoluene. When a small quantity of solid has separated, this is filtered off rapidly. The filtrate is diluted with water and the solid again crystallised from alcohol, and so on. Some little experience is required to judge the amount of solid which should be allowed to separate from the alcohol and acetic acid before filtering. The solid separating from alcohol should consist of sandy crystals (if fine needles separate the solution has been cooled too much and must be re-heated), which should melt not lower than 97° and the solid from acetic acid not lower than 104°. With these limits fairly large crops of crystals can be obtained, and the process is not unduly prolonged. The crops from alcohol are combined and crystallised from alcohol, when 3 : 4 : 6-trinitrotoluene is obtained pure. The crops from acetic acid are again crystallised from acetic acid and then from alcohol, when 2 : 3 : 4-trinitrotoluene is obtained. In these final crystallisations the solutions may be allowed to become quite cold.

In one experiment two portions of 225 grams of *m*-nitrotoluene were nitrated; 620 grams of mixed trinitrotoluenes were obtained (84 per cent.). Three crystallisations from alcohol and three from acetic acid followed by one crystallisation of the combined crops from alcohol and from acetic acid and alcohol respectively yielded 200 grams of pure 3 : 4 : 6-trinitrotoluene and 100 grams of pure 2 : 3 : 4-trinitrotoluene.

2 : 4-*Dinitromethyl*-m-*toluidine*.—Twenty grams of 2 : 3 : 4-trinitrotoluene are dissolved in 250 c.c. of hot alcohol, and a solution of [illegible] grams of methylamine hydrochloride in a small quantity of water is added, followed by 12 c.c. of ammonium hydroxide (D 0·880) drop by drop. As the ammonia is added, the liquid darkens, but rapidly turns to a clear, orange colour. The mixture is then boiled for a few minutes, cooled, and water added cautiously until crystallisation begins. The solid is washed with water to remove ammonium chloride and crystallised from alcohol, when 2 : 4-*dinitromethyl*-m-*toluidine* separates in long, flat, orange needles melting at 81°, readily soluble in hot and sparingly so in cold alcohol (Found, N = 19·7. $C_8H_9O_4N_3$ requi[illegible]

4 : 6-*Dinitromethyl*-m-*tol*[illegible] same as that of the above comp[illegible] toluene.

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Soon after the addition of the first drops of ammonia the compound begins to separate, and the addition of water during cooling is unnecessary. 4 : 6-*Dinitromethyl*-m-*toluidine* crystallises from boiling alcohol, in which it is sparingly soluble, in yellow needles melting at 173° (Found. N = 20·0. $C_8H_9O_4N_3$ requires N = 19·9 per cent.). This compound is possibly the same as that described by Wurster and Riedel (*Ber.*, 1879, **12**, 1800), who obtained it by the nitration of dimethyl-*m*-toluidine and found its melting point to be 168°. They regarded it, however, as a dimethyl derivative.

2 : 4-*Dinitrodimethyl*-m-*toluidine*.—Twenty grams of 2 : 3 : 4-trinitrotoluene in 250 c.c. of boiling alcohol are treated with 9 grams of dimethylamine hydrochloride and 12 c.c. of ammonium hydroxide. The mixture is diluted with two to three times its bulk of water and extracted with ether. After evaporating the dried ethereal extract, 2 : 4-*dinitrodimethyl*-m-*toluidine* remained as an orange, uncrystallisable oil.

4 : 6-*Dinitrodimethyl*-m-*toluidine*.—Ten grams of 3 : 4 : 6-trinitrotoluene in 100 c.c. of boiling alcohol are treated with 4·5 grams of dimethylamine hydrochloride and 6 c.c. of ammonium hydroxide. The mixture is cooled, diluted slightly with water, and the solid which separates crystallised from alcohol. 4 : 6-Dinitrodimethyl-*m*-toluidine separates in yellow needles, melting at 107°, more readily soluble in organic solvents than the corresponding monomethyl derivative. This compound has been prepared by Wurster and Riedel (*loc. cit.*) by the nitration of dimethyl-*m*-toluidine in acetic acid solution.

2 : 4 : 6-*Trinitrotolylmethylnitroamine*.—For the preparation of this compound 2 : 4- or 4 : 6-dinitro-methyl- or dimethyl-*m*-toluidines may be employed, or a mixture of these obtained by the action of crude methylamine hydrochloride containing dimethylamine on a mixture of 2 : 3 : 4- and 3 : 4 : 6-trinitrotoluenes. Forty grams of the compound are added in small quantities at a time to 100 c.c. of nitric acid (D 1·5) warmed to 50°. Copious red fumes are evolved, particularly when dimethyl derivatives are present, and when all the solid has been added the mixture is heated on the water-bath until the evolution of nitrous fumes ceases. The mixture is then cooled and water added, when trinitrotolylmethylnitroamine separates out, usually as an oil, which solidifies on keeping. The solid is washed thoroughly and crystallised from alcohol, to which a few drops of acetic acid have been added, or from a mixture of alcohol and benzene. Trinitrotolylmethylnitroamine has a remarkable tendency to separate from solvents in an oily condition, and considerable difficulty is generally experienced in crystallising it. When the solid is fused it supercools to a viscid mass in which

crystallisation is very slow, extending over months. Further, in the presence of alcohol, it is very sensitive to alkalis, much more so than trinitrophenylmethylnitroamine, and when crystallised from alcohol in glass vessels sufficient alkali is introduced to impart a faint violet tinge to the product. The addition of hard water to an alcoholic solution produces a marked colour in the product which crystallises out.

4 : 6-*Dinitrotolylmethylnitroamine.*—Five grams of 2 : 4-dinitromethyl-*m*-toluidine are added to 50 c.c. of nitric acid (D 1·42) warmed to 50°. The mixture is kept at 50° for five minutes and then filtered while hot through glass-wool, 20 c.c. of water are added, and the whole is cooled when the nitroamine separates out. 4 : 6-*Dinitrotolylmethylnitroamine* crystallises from acetone or water in yellow plates melting and decomposing at 157° (Found, N = 21·8. $C_8H_8O_6N_4$ requires N = 21·9 per cent.). This compound on further nitration with fuming nitric acid yields trinitrotolylmethylnitroamine. The nitro-group attached to nitrogen is removed by heating 1 gram with a solution of 0·5 gram of phenol in 20 c.c. of 80 per cent. sulphuric acid on the steam-bath for thirty minutes. The colour of the solution changes through blue to violet, and finally brown. After cooling, the mixture is poured into water, the solid which separates washed with ammonia and crystallised from acetone and alcohol with the addition of animal charcoal, when 4 : 6-dinitromethyl-*m*-toluidine is obtained and identified by the method of mixed melting points.

2 : 4-*Dinitrotolylmethylnitroamine.*—This compound is prepared in a similar manner to the above from 2 : 4-dinitromethyl-*m*-toluidine, and crystallises from alcohol in very pale yellow needles melting at 111° (Found, N = 21·8. $C_8H_8O_6N_4$ requires N = 21·9 per cent.).

On further nitration with fuming nitric acid it also yields 2 : 4 : 6-trinitrotolylmethylnitroamine, but when treated with phenol and sulphuric acid 2 : 4 : 6-trinitromethyl-*m*-toluidine is obtained and not 2 : 4-dinitromethyl-*m*-toluidine, as would be expected. The possibility of this substance being 2 : 4 : 6-trinitrotolylmethylnitrosoamine was eliminated by the preparation of this compound, which was found to be quite distinct. Apparently the nitro-group in 2 : 4-dinitrotolylmethylnitroamine migrates to the ring so readily in the presence of sulphuric acid owing to the para-position being free that this reaction takes place in preference to the nitration of the phenol by the nitroamino-group.

2 : 4 : 6-*Trinitrotolylmethylnitrosoamine.*—Six grams of 2 : 4 : 6-trinitromethyl-*m*-toluidine are suspended in 50 c.c. of glacial acetic acid and 30 c.c. of a 20 per cent. solution of nitrogen peroxide in

acetic acid added. The mixture becomes slightly warm, and the solid dissolves completely. Water is gradually added with thorough shaking, when a buff, granular precipitate is formed, which is crystallised from alcohol. 2 : 4 : 6-*Trinitrotolylmethylnitrosoamine* crystallises in pale buff, sandy crystals melting at 120° (Found, N = 24·8. $C_8H_7O_7N_5$ requires N = 24·6 per cent.).

2 : 4-*Dinitrotolylmethylnitrosoamine and* 4 : 6-*Dinitrotolylmethylnitrosoamine*.—These compounds are prepared in a similar manner to the above from 2 : 4- and 4 : 6-dinitromethyl-*m*-toluidine respectively. 2 : 4-*Dinitrotolylmethylnitrosoamine* crystallises from alcohol in colourless needles melting at 65° (Found, N = 23·5. $C_8H_8O_5N_4$ requires N = 23·3 per cent.). 4 : 6-*Dinitrotolylmethylnitrosoamine* crystallises from alcohol in brilliant, yellow needles melting at 94° (Found, N = 23·6. $C_8H_8O_5N_4$ requires N = 23·3 per cent.).

2 : 4 : 6-*Trinitromethyl*-m-*toluidine*.—It was not found possible to regulate the conditions of nitration of the dinitromethyl-*m*-toluidines so as to obtain this compound directly. It may, however, be prepared from these compounds by nitrating them first to trinitrotolylmethylnitroamine and removing the nitro-group attached to the nitrogen atom. Five grams of the nitroamine are added in small portions at a time to a solution of 4 grams of phenol in 50 c.c. of 80 per cent. sulphuric acid at 50°, and the temperature is cautiously raised to 90°. After heating at 90° for thirty minutes the product is treated as in the denitration of 4 : 6-dinitrotolylmethylnitroamine (see above), and the 2 : 4 : 6-trinitromethyl-*m*-toluidine crystallised from a mixture of acetone and alcohol. This compound is identical with that obtained by Blanksma (*loc. cit.*) by the action of methylamine on 2 : 4 : 6-trinitrotolyl methyl ether.

The authors wish to express their thanks to the Director of Artillery for permission to publish these results.

RESEARCH DEPARTMENT,
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WOOLWICH.

[*Received, December 8th*, 1920.]

XII.—*Organic Derivatives of Tellurium. Part III. Crystallographic and Pharmacological Comparison of the α- and β-Dimethyltelluronium Dihaloids.*

By Isabel Ellie Knaggs and Richard Henry Vernon.

Of the six dimethyltelluronium dihaloids, the two iodides were the most suitable for crystallographic investigation, which was carried out by one of us (I.E.K.) in the Mineralogical Department under the direction of Mr. A. Hutchinson.

α- or "trans"-*Dimethyltelluronium Di-iodide*, ${}^{I}_{Me}{>}Te{<}^{Me}_{I}$.

This was prepared in the usual manner, and the large crystals from chloroform or benzene were examined.

Crystal System.—Monoclinic. Class: holohedral. Axial angle = 72°21′. Axial ratio: $a:b:c = 0{\cdot}5578:1:0{\cdot}4310$.

Forms Observed.

$A = \{100\}$, $B = \{010\}$, $C = \{001\}$, $k = \{20\bar{1}\}$, $m = \{110\}$, $m' = \{120\}$, $m'' = \{130\}$, $q = \{011\}$, $l = \{021\}$, $o = \{111\}$, $o' = \{\bar{1}11\}$, $n' = \{\bar{1}21\}$.

Table of Angles.

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.	Difference.
$A : C = (100) : (001)$	2	72°21′ —72°21½′	72°21′	72°21′	0′
$C : k' = (001) : (\bar{2}01)$	6	70°2′ —70°14′	70°9′	*	—
$k' : A' = (\bar{2}01) : (\bar{1}00)$	3	37°26′ —37°34′	37°30′	*	—
$B : m'' = (010) : (130)$	7	32°3½′ —32°27′	32°12′	32°6′	6′
$B : m' = (010) : (120)$	18	43°10′ —43°24′	43°16′	*	—
$B : m = (010) : (110)$	14	61°48′ —62°10½′	62°2′	62°1′	1′
$B : q = (010) : (011)$	8	67°17′ —67°44′	67°39′	67°39′	0′
$B : l = (010) : (021)$	6	50°30′ —50°46′	50°37′	50°34½′	2½′
$C : m = (001) : (110)$	5	74°28′ —74°31′	74°30′	74°22′	8′
$C : o = (001) : (111)$	5	34°19′ —34°22′	34°20′	34°21′	1′
$B : o = (010) : (111)$	9	73°58½′—74°10½′	74°5′	74°3′	2′
$q : n' = (011) : (\bar{1}21)$	2	40°26′ —40°33′	40°31′	40°31′	0′
$n' : m = (\bar{1}21) : (\bar{1}10)$	2	53°29′ —53°31′	53°30′	53°27′	3′
$A : o = (100) : (111)$	2	44°3′	44°3′	43°56′	7′
$o : q = (111) : (011)$	8	29°31′ —29°52′	29°45′	29°47′	2′
$q : o' = (011) : (\bar{1}11)$	2	40°35½′—40°47′	40°41′	40°37½′	3½′
$m' : n' = (\bar{1}20) : (\bar{1}21)$	13	78°1′ —78°22′	78°9′	78°10′	1′
$n' : k' = (\bar{1}21) : (\bar{2}01)$	13	44°41′ —45°0′	44°51′	44°50′	1′
$k' : m' = (\bar{2}01) : (\bar{1}20)$	21	56°29½′—57°14′	57°3′	57°0′	3′
$C : n' = (001) : (\bar{1}21)$	1	55°18′	55°18′	55°14′	4′
$B : n' = (010) : (\bar{1}21)$	3	52°19′ —52°24′	52°22′	52°16′	6′
$n' : o' = (\bar{1}21) : (\bar{1}11)$	2	16°33′	16°33′	16°34′	1′
$m : k' = (\bar{1}10) : (\bar{2}01)$	3	45°28½′—45°35′	45°33′	45°31′	2′

Habit.—Short, prismatic, terminated at either end by a large macrodome, k, and by a variable number of smaller domes and pyramids (Fig. 1).

Cleavage.—None observed.

Specific Gravity.—Determined by weighing in water, D_4^{14} 3·338 (corrected).

Topic Axes.—$\chi : \psi : \omega$ = 4·537 : 8·133 : 3·506.

Optical Characters.—Refractive index, high. By immersion method, greater than 1·74. On looking through a crystal perpendicular to B, strong pleochroism was observed, the colour changing from light red to very dark red. The maximum absorption of light takes place for vibrations parallel to the extinction direction, which makes an angle of 4½° with the vertical axis, Z, in the acute axial angle. It was not possible to obtain an optic picture in convergent light owing to the great absorption.

β- or "cis"-*Dimethyltelluronium Di-iodide*, $\begin{matrix}I\\I\end{matrix}{>}Te{<}\begin{matrix}Me\\Me\end{matrix}$.

This was prepared from the β-base and crystallised from methyl alcohol. The crystals examined were small, but well defined. In reflected light they had a black, metallic lustre.

Crystal System.—Monoclinic. Class: holohedral. Axial angle = 76°52′. Axial ratio: $a:b:c$ = 0·5465 : 1 : 0·4222.

Forms Observed.

$A = \{100\}$, $B = \{010\}$, $C = \{001\}$, $m = \{110\}$, $q = \{011\}$, $o' = \{\bar{1}11\}$, $n' = \{\bar{1}21\}$.

Table of Angles.

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.	Difference.
$A : C$ = (100) : (001)	7	76°50′ —77°31′	77°16′	76°52′	24′
$B : m$ = (010) : (110)	18	61°48′ —62°8′	61°59′	*	—
$C : q$ = (001) : (011)	9	22°5½′ —22°34′	22°18′	22°21′	3′
$q : n'$ = (011) : ($\bar{1}$21)	5	38°23½′—39°20′	38°55′	39°8½′	13½′
$n' : m$ = ($\bar{1}$21) : ($\bar{1}$10)	5	51°6′ —51°25′	51°15′	*	—
$C : n'$ = (001) : ($\bar{1}$21)	6	52°53′ —53°59′	53°27′	53°31′	4′
$B : n'$ = (010) : ($\bar{1}$21)	18	53°21′ —53°47½′	53°37′	*	—
$n' : o'$ = ($\bar{1}$21) : ($\bar{1}$11)	8	15°55½′—16°10′	16°2½′	16°8½′	6′
$A : n'$ = (100) : (12$\bar{1}$)	5	67°2′ —67°14′	67°7½′	66°50′	17½′

The habit is characterised by the small development of the prism faces, $m\{110\}$, and by the large development of the form $n'\{\bar{1}21\}$. Faces of the forms $C\{001\}$, $o'\{\bar{1}11\}$, and some small dome faces are also present (Fig. 2).

Had the β-crystals alone been under consideration, it would have been natural to regard the faces of the forms {$\bar{1}$21} and {$\bar{1}$11} as prisms having indices {120} and {110} respectively. In order, however, to bring out the relationship which exists between the α- and β-crystals, it was found necessary to adopt the orientation given above.

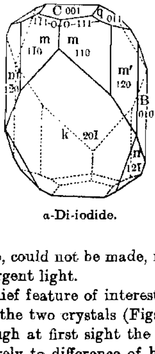
Cleavage.—None observed.

Specific Gravity.—Determined by weighing in water, $D_4^{14} = 3{\cdot}305$ (corrected).

Topic Axes.—$\chi : \psi : \omega = 4{\cdot}488,\ 8{\cdot}214,\ 3{\cdot}468$.

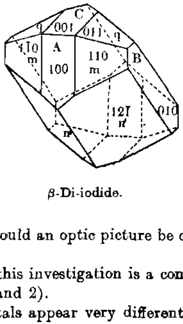
Optical Characters.—Refractive index: high; as found by the immersion method, greater than 1·74. Absorption: very high, the crystals being nearly opaque. Observations as to the pleochroism,

FIG. 1.



α-Di-iodide.

FIG. 2.



β-Di-iodide.

herefore, could not be made, nor could an optic picture be obtained n convergent light.

The chief feature of interest in this investigation is a comparison between the two crystals (Figs. 1 and 2).

Although at first sight the crystals appear very different, this is lue entirely to difference of habit. In reality, a large number of orms, {001}, {011}, {110}, {010}, {$\bar{1}$21}, are common to each ubstance, and the angles in the prominent zones and the axial atios show striking similarity. This is most marked in the zones]10,110], [010,011], in which the angles are almost identical, and he divergence is greatest in the zone parallel to the diad axis of ymmetry, the acute axial angles differing by as much as 4½ degrees. 'he close similarity of form also finds expression in the topic axes, he values of χ and ω for the β-compound being slightly less, and hat of ψ slightly greater, than is the case for the α-compound.

The difference of habit is mainly due to the large development

of $k\{20\bar{1}\}$ in the α-compound and its absence in the β-compound, in which $n'\{\bar{1}21\}$ plays a prominent part.

The similarity of the two forms is so close that they stand to one another much in the same relation as the members of an isomorphous series. The small size of the crystals, their opacity, and high refractive index have precluded a detailed comparison of their optical properties, nor has it been found possible to prepare mixed crystals containing both compounds.

In marked contrast to the similarity in crystalline structure of the α- and β-iodides is the totally different physiological behaviour of the α-haloids as compared to the corresponding β ones.

The iodides were not used for the pharmacological investigation, as they are insoluble in water, but the chlorides and bromides were eminently suitable for this purpose.

Dr. W. E. Dixon, who is still investigating these substances, and will shortly publish a full statement of his results in an appropriate journal, has kindly sent the following note:

"Both these organic compounds of tellurium when taken into the animal body are excreted from the lungs as dimethyl telluride, a substance which exerts little physiological action apart from its odour.

"Before this change occurs in the body, the α- and β-compounds exert specific actions of an entirely different nature. The former slows and weakens the heart, and the blood-pressure falls. It also stimulates plain muscle, particularly that of the uterus and intestine, to increased activity. Its action on the central nervous system is almost negligible.

"The β-compound has the most profound stimulant action on the medulla, giving rise to an increase of blood-pressure and *increasing the depth and rapidity of respiration. Generally before* the blood-pressure has reached the normal again, a second rise occurs; this is due to the liberation of adrenalin from the supra-renal glands, upon which the β-compound exerts a unique and specific effect not comparable with that produced by any other known chemical. Large doses of the β-compound, such as 60 milligrams to a cat, paralyse the whole nervous system—brain, spinal cord, and motor nerves."

University Chemical Laboratory,
Cambridge.

[*Received, December* 17*th*, 1920.]

XIII.—*The Rôle of Protective Colloids in Catalysis. Part I.*

By Thomas Iredale.

The effect of protective colloids in inhibiting the catalytic decomposition of hydrogen peroxide by colloidal platinum has already been noted by Gróh (*Zeitsch. physikal. Chem.*, 1914, **88**, 414), who found that they appeared to follow the order of Zsigmondy's "gold number" series (*Zeitsch. anal. Chem.*, 1901, **40**, 697; "Colloids and the Ultramicroscope," 1914, 79) in their activity in this respect. It appeared desirable, however, to extend investigations in this direction, as the experimental results obtained by Gróh were too few to permit of a general statement as to the relative effects of different protective colloids. A number of these colloids have now been examined in this regard, and it has been found that, in general, the stronger a substance is as a protective colloid the greater will be its inhibition of catalytic activity, and that a substance like sucrose, which is without protective effect, is likewise without inhibitive effect.

Now in view of the circumstances in which the protective colloids are examined in the two cases—Zsigmondy's coagulation method and Gróh's catalytic method—there is nothing altogether surprising in these results. From superficial considerations they might almost be anticipated, and the author was inclined to believe that they might throw considerable light not only on the mechanism of protective action, but also on the processes involved in the hydrogen peroxide decomposition. Unfortunately, owing to war conditions, Gróh's paper itself was not available, and the author had to be content with abstracts (A., 1915, ii, 239; *Chem. Abstracts*, 1915, 7). From these it does not appear that Gróh advanced any thorough argument to account for his results, but he seems to have endeavoured to obtain a relation between the gold number of protective colloids and the extent of their inhibitive effect, the significance of which seems, at present, a little obscure.

It is necessary to examine the analogy more thoroughly. In this connexion some recent remarks made by workers in this field are of interest. Bancroft (*J. Physical Chem.*, 1917, **21**, 775) considers that a substance like gelatin may increase the degree of dispersity of the catalyst, thus exposing a larger surface with increased catalytic activity, but that this effect may be more than counterbalanced by the presence of the gelatin itself, which hinders the

adsorption of the hydrogen peroxide. There is no evidence that protective colloids increase the degree of dispersity of a metal sol already formed, and in view of Rusznyak's work (*Zeitsch. physikal. Chem.*, 1913, **85**, 681) on the decreased catalytic activity with increased dispersity, Bancroft's argument seems scarcely reasonable.

Rideal (*J. Amer. Chem. Soc.*, 1920, **42**, 749) considers that diffusion is the chief factor concerned in the rate of decomposition of hydrogen peroxide, and argues against the idea of a colloid-complex formation. If this is the case, why should a strong protective colloid inhibit to a greater extent than a weak one? What part can diffusion play in the ordinary method of measuring the value of protective colloids as announced by Zsigmondy? The change from red to blue in the colour of gold sols is assumed to be due to a union of the gold particles after their charges have been neutralised by the adsorption of certain ions. Protective colloids may hinder this change for one or other of two reasons. It may be that after the neutralisation of their charges the gold particles are prevented from uniting owing to the presence of the protective colloid. On this theory it is difficult to see where the analogy exists in the case of the catalytic process. If we assume, however, that the protective colloid hinders the adsorption of the ions that would bring about the coagulation, then the analogy is quite complete. The rate of decomposition of hydrogen peroxide is probably determined by a number of factors of which adsorption is undoubtedly one of the chief. Anything which hinders the adsorption of the hydrogen peroxide by the catalyst will retard the velocity of reaction as measured in the usual way, and a strong protective colloid which hinders the adsorption of ions better than a weak one, may also hinder the adsorption of the hydrogen peroxide more efficiently. It remains to be seen, however, if the gold number is really expressive of these relations.

Zsigmondy ("Colloids and the Ultramicroscope," 1914, 150) has endeavoured to follow the mechanism of protective action under the ultramicroscope. The assumed union of the gold and gelatin ultramicrons is followed by decreased mobility in the former, except at a certain concentration of gelatin, below which there does not seem to be any retardation in the movements of the gold particles. It will be seen later that the inhibitive effect of gelatin is noticeable at much lower concentrations than the critical one mentioned by Zsigmondy, and this inhibition cannot be due, therefore, to any decreased mobility in the particles of the catalyst. As far as the Brownian movement is concerned, however, the part played by it in the catalysis is still somewhat obscure.

Bredig (*Zeitsch. physikal. Chem.*, 1901, **37**, 14) has shown that the adsorption of poisons by the catalyst follows the logarithmic law, and it was anticipated that the adsorption of protective colloids might also obey the same law. From results obtained with gelatin at very low concentrations, it appears that the process is more complicated than a simple calculation can possibly account for, owing to the continual subdivision of the gelatin ultramicrons over a certain range of dilution.

The results of experiments on the poisoning of protected metals will be made available in a later communication.

EXPERIMENTAL.

The hydrogen peroxide used in all these experiments was carefully purified by distillation under diminished pressure. The colloidal platinum solutions were prepared by Bredig's method, using a current of 110 volts and 10—12 amperes, the temperature of the water being kept below 25°. Solutions made by this method may be diluted to the extent desired, and after allowing the larger particles to settle, may be used directly without filtering. They appear, however, to be much more sensitive than filtered ones, and cannot be used for very exact work where it is desired to follow the course of a reaction with the maximum of accuracy. The velocity constant falls slightly during the reaction, instead of rising, as is usually the case.

The solutions of protective colloids were prepared by simple dissolution of the materials in water, adopting the usual procedure for gelatin and starch. In the case of gum tragacanth and egg-albumin, which gives extremely turbid solutions, a known weight of material was dissolved as much as possible in water, and the amount of undissolved matter ascertained after filtration. With a knowledge of the weight of substance in the filtrate it could then be diluted to the concentration required. The concentration of protecive colloids when first prepared was 0·04 per cent., and lower concentrations were obtained merely by dilution from this strength.

The initial concentration of the hydrogen peroxide in all the experiments was $M/40$. The concentration of the platinum solutions was the same throughout any one series.

All the reactions were carried out at 25°, and in every instance the platinum solutions on admixture with the protective colloids were allowed to remain for fifteen minutes at the temperature of the experiment before the addition of the hydrogen peroxide. At different intervals 10 c.c. of the reaction mixture were titrated, after addition to dilute sulphuric acid, with standard permanganate

(about $N/40$). It was not found necessary to apply a correction to the titrations for organic matter present as the concentration of the latter was apparently too small to affect the results.

The velocity constant was calculated from the usual formula:

$$k = 0\cdot4343\ k_1 = \frac{1}{t}\log_{10}\frac{a}{a-x}$$

(t in minutes, and $a-x$ in terms of c.c. of potassium permanganate).

The values of k given in the tables are the progressive ones obtained during any reaction, and the mean of these in each case gives the same result on comparison as the time for 50 per cent. decomposition.

The ratio values were calculated by taking the velocity constant with unprotected metal as unity.

TABLE I.

Protective Colloid Preparations: Six Days Old.

Series.	Protective colloid.	k.			Mean.	Ratio.
I.	none	0·026,	0·023,	0·023	0·024	1
	0·01% gelatin	0·0043,	0·0043,	0·0044	0·0043	0·17
	„ glue	0·0046,	0·0043,	0·0041	0·0043	0·17
	„ egg-albumin	0·0055,	0·0052,	0·0050	0·0052	0·22
	„ gum arabic	0·014,	0·012,	0·012	0·013	0·54
	„ sucrose	0·027,	0·025,	0·025	0·025	1
II.	none	0·039,	0·038,	0·037	0·038	1
	0·001% gelatin	0·0074,	0·0082,	0·0078	0·0078	0·20
	„ glue	0·0080,	0·0078,	0·0077	0·0078	0·20
	„ egg-albumin	0·013,	0·012,	0·012	0·012	0·32
	„ gum arabic	0·032,	0·031,	0·031	0·031	0·82
	„ sucrose	0·038,	0·036,	0·036	0·037	1

TABLE II.

Preparations One Day Old.

Series.	Protective colloid.	k.			Mean.	Ratio.
I.	*none*	*0·057,*	*0·052,*	*0·056*	*0·055*	*1*
	0·01% gelatin	0·0058,	0·0061,	0·0060	0·0059	0·11
	„ glue	0·0071,	0·0073,	0·0071	0·0072	0·13
	„ egg-albumin	0·0093,	0·0095,	0·0094	0·0094	0·17
	„ gum arabic	0·037,	0·035,	0·034	0·035	0·64
II.	none	0·025,	0·024,	0·025	0·025	1
	0·001% gelatin	0·0044,	0·0043,	0·0045	0·0044	0·18
	„ glue	0·0055,	0·0059,	0·0053	0·0056	0·22
	„ egg-albumin	0·0068,	0·0072,	0·0071	0·0070	0·28
	„ gum arabic	0·020,	0·021,	0·020	0·020	0·80

From these results it is evident that the inhibitive effect is in the order gelatin and glue>egg-albumin>gum arabic>sucrose, which does not appear to affect the reaction at all.

This order is also followed in Zsigmondy's coagulation experiments, but the author has not been able to discover any exact relationship between the gold numbers of these colloids and their inhibitive activity as indicated in the ratio table.

Subsequent determinations of the gold number by the usual method (Zsigmondy, *loc. cit.*) gave values of 0·006 and 0·008 for the samples of gelatin used, and 0·2 for gum arabic, so that the author was not working with materials showing any great anomalies in this respect.

The gold numbers seem, therefore, to be only a useful guide to enable one to predict the probable order of inhibitive activity.

The protective colloids are themselves without appreciable action on hydrogen peroxide. Bredig (*Zeitsch. physikal. Chem.*, 1899, **31**, 342) showed this in the case of gelatin, and it has been found that the stability of a hydrogen peroxide solution is *not* appreciably affected by the addition of protective colloids of the concentrations indicated in any of these tables.

The extent of the inhibition produced by some of the weaker protective colloids is shown in the following table:

TABLE III.

Preparations Two Days Old.

Series.	Protective colloid.	*k*.			Mean.	Ratio.
I.	none	0·080,	0·083,	0·086	0·083	1
	0·01% gum tragacanth	0·030,	0·029,	0·027	0·028	0·34
	,, dextrin	0·032,	0·031,	0·030	0·031	0·37
	,, starch	0·042,	0·042,	0·040	0·041	0·50
	,, gum arabic	0·044,	0·044,	0·040	0·043	0·52
II.	none	0·017,	0·018,	0·018	0·018	1
	0·01% egg-albumin	0·0036,	0·0038,	0·0039	0·0038	0·21
	,, tragacanth	0·0078,	0·0074,	0·0073	0·0075	0·42
III.	none	0·017,	0·018,	0·019	0·018	1
	0·001% egg-albumin	0·0057,	0·0058,	0·0056	0·0057	0·32
	,, tragacanth	0·012,	0·013,	0·013	0·013	0·72
IV.	none	0·017,	0·018,	0·019	0·018	—
	0·01% sodium oleate	0·021,	0·023,	0·023	0·023	—
	0·005% ,, ,,	0·0130,	0·0130,	0·0131	0·0130	—
	0·001% ,, ,,	0·0127,	0·0129,	0·0127	0·0128	—
	0·0025% ,, ,,	0·0150,	0·0152,	0·0151	0·0151	—

From these results it is evident that tragacanth inhibits to a less extent than egg-albumin, but is somewhat more effective than dextrin, which is more effective than starch and gum arabic.

Sodium oleate behaves abnormally, as it must be completel hydrolysed at these low concentrations, and the velocity constan will rise owing to the presence of hydroxyl ions. It is interesting t observe, however, that on dilution from 0·01 per cent. concentra tion the protective effect of the soap begins to dominate the situa tion, and the velocity constant therefore falls, but rises again o further diIntion of the protective colloid. This observation is o great importance, as it shows that the protective action of soaps o gold sols is not due to the stabilising effect of the hydroxyl ion alone—the concentration of the latter in a 0·01 per cent. sodiun oleate solution could not be greater than $N/3000$—but more prob ably in greater part to the acid–soap residue which is more complex perhaps, than is generally realised.

Gelatin appears to be active as an inhibitor at extremely lov concentrations. With a platinum solution of medium concentra tion (about 1/30,000 gram-atoms per litre) the following result were obtained:

TABLE IV.

Series.	Protective colloid.	*k*.	Mean.
I.	none	0·0148, 0·0152, 0·0151, 0·0154	0·0151
	0·005% gelatin	0·0028, 0·0026, 0·0026, 0·0027	0·0027
	0·001% ,,	0·0032, 0·0032, 0·0031, 0·0029	0·0031
	0·0001% ,,	0·0045, 0·0044, 0·0041, 0·0040	0·0043
	0·00005% ,,	0·0050, 0·0049, 0·0050, 0·0051	0·0050
	0·00001% ,,	0·0105, 0·0108, 0·0108, 0·0108	0·0107
	0·000005% ,,	0·0137, 0·0142, 0·0141, 0·0139	0·0140
	0·000001% ,,	0·0149, 0·0148, 0·0152, 0·0154	0·0151
II.	none	0·0158, 0·0161, 0·0167, 0·0162	0·0162
	0·001% gelatin	0·0030, 0·0032, 0·0030, 0·0029	0·0030
	0·0001% ,,	0·0043, 0·0039, 0·0038, 0·0038	0·0039
	0·00005% ,,	0·0050, 0·0047, 0·0045, 0·0047	0·0048
	0·00001% ,,	0·0108, 0·0110, 0·0114, 0·0117	0·0112
	0·000005% ,,	0·0123, 0·0123, 0·0129, 0·0133	0·0127
	0·000001% ,,	0·0155, 0·0156, 0·0159, 0·0160	0·0158

Series I and II were carried out with different samples o gelatin.)

The most striking fact about these results is the gradual rise o the velocity constant with diminishing gelatin concentrations dowr to 0·00005 per cent., and the rapid rise on further dilution of the protective colloid.

Now Menz (*Zeitsch. physikal. Chem.*, 1909, **66**, 129) found that the protective action of gelatin increased on dilution, hut the results were usually dependent on the mode of preparation of the origina solution. It seems not improbable, however, that on diluting a gelatin solution of low concentration, the larger gelatin ultra microns split into smaller ones, and these heing more strongly

adsorbed by the gold or platinum particles will partly make up for the decreased concentration of the protective colloid. Hence the velocity constant will only rise very slowly until this subdivision process ceases, when further dilution of the protective colloid will now bring about its more rapid elevation.

Summary.

(i) The inhibitive effect of protective colloids on the catalytic decomposition of hydrogen peroxide by colloidal platinum has been examined in a number of instances.

(ii) It has been found that the stronger a substance is as a protective colloid the greater will be its inhibition of catalytic activity.

(iii) In the case of a strong protective colloid like gelatin, the inhibitive effect is noticeable at very great dilution, for example, 0·000005 per cent., or one part in twenty million parts of water.

(iv) The inhibition is explained on the ground of selective adsorption resulting in a decreased concentration of hydrogen peroxide at the platinum surface, and a consequent fall in the value of the velocity constant.

(v) There is no precise relation between the gold numbers of protective colloids and the extent of their inhibition.

(vi) The reaction may be used not only to detect adsorption effects, but probably, also, changes in state of the protective colloid owing to the subdivision of its ultramicrons.

I am indebted to the Committee on award of Science Research Scholarships in this State for a scholarship which has enabled me to carry out this investigation.

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XIV.—*Yeast Crops and the Factors which Determine them.*

BY ARTHUR SLATOR.

MANY investigations have been carried out to determine the factors which influence the amount of yeast produced by growth in a suitable medium, and much of the important earlier work on the subject is published in these *Transactions*. It has been shown in

recent years that the growth of micro-organisms under simple conditions follows the exponential law of increase, and equations expressing growth and fermentation have been worked out and experimentally verified. In this communication an attempt has been made to express yeast crops in terms of generation-times and fermentative activity of the yeast and to use such equations to test some of the generally accepted views on the subject. The reproduction of yeast in a medium such as malt wort takes place in definite phases. A period of quiescence (lag phase in growth) is followed by unrestricted growth (logarithmic phase in growth), which continues until retarding influences, such as lack of necessary food or the production of toxins, come into play. Growth finally ceases when these retarding influences become sufficiently great. Under the usual conditions of yeast growth and alcoholic fermentation several factors play a part in limiting growth, but a simple case where one factor only determines the total growth will be first discussed.

Conditions can be so arranged that the sugar in the medium can be made this limiting factor. All other foods must be in large excess, and substances toxic to growth must not be allowed to accumulate. The crop then admits of calculation in the following manner.

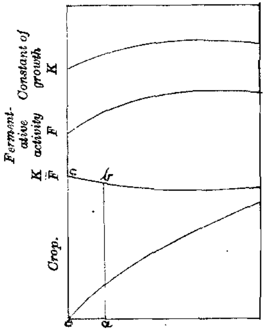
It has been shown (Slator, *Bio-Chem. J.*, 1913, **7**, 198) that during the logarithmic period of growth the ratio of the increase in the number of cells n to the amount of sugar s fermented is a constant, and that this ratio $\frac{n}{s} = \frac{K}{F}$, where K is the constant of growth and F is the fermentative activity of the yeast. During later stages in growth, K and F may not remain constant, but at any given time they have definite values, and the small increments in the yeast and sugar fermented are determined by the equation $\frac{dn}{ds} = \frac{K}{F}$.

We have therefore $n = \int \frac{K}{F} ds$ + constant. Yeast crops (from a small seeding) are therefore determined by the way this ratio K/F varies with different concentrations of sugar. A graphical method of calculation of such crops is shown in Fig. 1. The values of K and F are obtained experimentally and plotted against the corresponding concentration of sugar. The K/F curve is then constructed. The crop obtained during the complete fermentation of "a" grams of sugar is represented by the area $oabc$. A curve can now be constructed showing yeast crops with various initial concentrations of sugar.

This theoretical curve should coincide with the experimental one *as long as the sugar is the limiting factor determining the final* crop. In the case described in the experimental part of this paper the ratio K/F is almost constant, and the crop is approximately proportional to the initial concentration of the sugar.

This method of calculating yeast crops is of general application, and a *similar* diagram can be constructed when other limiting factors are predominant. The other factors discussed in this paper are those relating to the seeding, oxygen, carbon dioxide, and temperature. Only a brief reference is made to the important influence which nitrogenous food can exert on yeast crops.

FIG. 1.



The influence of the amount of seeding admits of simple calculation if no change in the limiting factor takes place owing to change in the amount of seeding. The ratio K/F is independent of the number of yeast cells: the growth under definite conditions should therefore be a constant. The yeast crop is the sum of the seeding and the growth, the latter being constant. That this relationship holds good was first shown by A. L. Stern (T., 1901, **79**, 943; *J. Inst. Brewing*, 1902, **8**, 690). A. J. Brown had previously drawn the conclusion that the final yeast crop is almost independent of the amount of the seeding, and dednced the idea of a non-multiplying limit to yeast growth (T., 1892, **61**, 369). H. T. Brown considers the cell increase of most importance (*Ann. Botany*, 1914,

28, 197). There would probably be general acceptance of the idea of a constant cell increase under constant conditions if it were not for the fact that large seedings of yeast refuse to bud or show only a small increase (A. J. Brown, *loc. cit.*). A satisfactory explanation of this abnormality is given here. It was found that if actively growing yeast cells are used for seeding, the normal increase takes place even though the seeding is very large. Quiescent yeast cells pass through a lag phase before active growth occurs, and if retarding influences accumulate quickly the yeast never passes out of its quiescent state. Abnormally low crops are sometimes observed if very small seedings are used. Many investigators have noticed this effect (compare Lampitt, *Bio-Chem. J.*, 1919, **13**, 461). If actively growing yeast is used for seeding, this abnormality partly disappears, and the effect is probably connected with the lag phase in growth.

Much of the interest in yeast growth centres round the favourable influence which atmospheric oxygen has on the growth of the organism. Although it is more than 40 years since Pasteur's work on the subject appeared, there is still much diversity of opinion as to the method by which air acts. A. J. Brown (T., 1905, **87**, 1395) drew the conclusion that the development of yeast in malt wort is determined by the oxygen initially dissolved in the wort. H. T. Brown (*Ann. Botany*, 1914, **28**, 197) considers that the growth can be attributed to oxygen absorbed by the yeast used for seeding. It is possible, however, that these experimental results can be interpreted in other ways. Carbon dioxide retards yeast growth to a much greater extent than is recognised in these experiments. Moreover, yeast growth takes place under anaerobic conditions, although the cells have lost all their "oxygen charge" (see table IX). Euler and Lindner ("Chemie der Hefe," Leipzig, 1915) summarise the work of Pasteur, Chudiakow, Buchner and Rapp, Delbrück and others on the subject. They recognise the retarding influence of carbon dioxide on growth, and conclude that oxygen accelerates the growth of the yeast cells. One of the arguments against this view is the fact that growth in its simplest form is not accelerated by air or oxygen. Unrestricted growth is appreciably retarded by oxygen (see table V). In a short summary of the factors which influence growth (*J. Soc. Chem. Ind.*, 1919, **38**, 391 R), the view (previously discussed by other authors) is taken that malt wort contains a substance which easily gives up its oxygen to the yeast and that this substance accounts for growth under anaerobic conditions. Attempts were made to verify this assumption by estimating yeast crops under conditions that the unknown substance would become the limiting factor determining

the crop. The experiments were unsuccessful and this explanation appears to be incorrect. The matter has been reconsidered in the light of these experiments and the following interpretation is advanced. It is considered that there are two different modes* of growth of yeast, each involving a different set of chemical reactions. *The initial stages of growth in malt wort illustrate the one mode* of growth. Oxygen, either free or combined, or absorbed by the yeast, plays no part in the process. Free oxygen slightly retards this growth. The energy necessary for growth is obtained from the fermentation of the sugar. Carbon dioxide retards the growth, and if air is passed through the fermenting wort, yeast growth is increased owing to the displacement of carbon dioxide. Growth in lactose yeast water illustrates the other mode of growth. This growth is unaccompanied by alcoholic fermentation, but zymase is present in the cells. Free oxygen is here essential to growth, and if absent hardly any growth occurs. The necessary energy is obtained through some oxidation reaction carried out by the yeast. Carbon dioxide in large amounts also retards this growth. The factors determining which mode of growth takes place wheu both are possible have not yet been eompletely investigated. The available nitrogenons food is probably of importance, for whilst yeast growth in wort is not influenced by air at the beginning of the reaction, yeast growth in a medium prepared from half-fermented wort is favourably influenced by air (Slator, *Bio-Chem. J.*, *1918*, **12**, *254*).

Whilst the influence of large amounts of air on yeast growth admits of explanation on these lines, the influence of small amounts is less easy to understand. A wort saturated with air produces a larger yeast crop than one which contains no air.

The increase is out of all proportion to what would be expected from the amount of air available.† A number of experiments were carried out to obtain further information on the subject. It was found that if fermentation and yeast growth occur under conditions that supersaturation of the wort with carbon dioxide takes place the effect is readily verified. If, however, care is taken to control the concentration of the carbon dioxide the

* *Pasteur considered yeast to be an organism endowed with two modes of* life, and the theory advanced here agrees in some respects with that of Pasteur. The aerobic growth in lactose yeast water was investigated by Pasteur, and the view that this growth depends on air has been confirmed. The very slight growth under anaerobic conditions is probably due to a trace of fermentable sugar.

† According to H. T. Brown's figures, 1 c.c. of oxygen dissolved in wort causes the growth of 6000×10^6 yeast cells. Experiments in sealed tubes showed less than 100×10^6 cell increase for each c.c. of oxygen.

effect disappears. The conclusion is drawn that the influence of dissolved air is only indirect, and doubts are cast on the usually accepted explanation of the matter, namely, that the effect is *due to the favouring influence of the dissolved oxygen*. It is possible that supersaturation by carbon dioxide is lessened by the presence of dissolved air and that larger yeast crops are a consequence of this influence. The work of Findlay and King (T., 1913, **103**, 1170) on the rate of evolution of gases from supersaturated solutions is of much interest in this connexion.

Many of the arguments advanced in this publication depend on the assumption that carbon dioxide retards yeast growth. That the gas has this effect was considered to be the case by Delbrück (1886) and Foth (1887). (For a summary of the work see Delbrück and Hayduck, "Die Gärungsfuhrung," 1911, Berlin.) The correctness of these conclusions is accepted in this paper, but it is considered that the effect is more far-reaching than either these investigators or others have realised. A. J. Brown (T., 1905, **87**, 1406) concluded that carbon dioxide had no such effect, and that the retarding influence attributed to the gas was due to exclusion of oxygen. The experiments, however, are not conclusive, for no precautions are taken to remove the carbon dioxide formed during fermentation. Measurements of rates of growth in wort and in wort saturated with carbon dioxide show a very marked retarding influence of the gas. Some measurements of yeast crops grown under conditions that carbon dioxide becomes the limiting factor confirm these results in an interesting manner (see table IV). The influence of temperature on yeast crops is small (compare Stern, *J. Inst. Brewing*, 1902, **8**, 694). Both K and F have temperature-coefficients not greatly different from each other. If, therefore, the sugar is the factor controlling growth, the crops which depend on the ratio K/F will be almost independent of temperature (see table XI). This has been experimentally verified.

A publication by Carlson (*Biochem. Zeitsch.*, 1913, **57**, 513) is of much interest. Measurements of yeast growths and yeast crops in wort are made. The wort is kept continually stirred and the amount of yeast in suspension estimated by centrifuging, a method adopted here. If allowance is made for the fact that Carlson's wort is saturated with carbon dioxide, the conclusions regarding rates of growth are in general agreement with those given here and in previous papers. His method of treating yeast crops is less easy to follow, for no precaution is taken to make a single factor the limiting one which determines the crop; moreover, it is unlikely that the relationship between concentration of food supply and growth is as simple as is assumed.

The question whether any food accessory substance (vitamin) is necessary to yeast growth has been considered in so far as it affects the experiments described here. No evidence of the necessity of such a substance was forthcoming, for heating the wort to a high temperature and filtering through Fuller's earth caused no decrease in the value of the wort as a medium for growing yeast.

Experimental.

Methods of Estimating Concentrations of Yeast.

Two methods were employed in this investigation to estimate the amount of yeast suspended in a liquid. When the amount was greater than a few million per c.c. it was estimated by centrifuging and measuring the quantity of deposit. The straight 5 cm. graduated capilliary tube used for blood analysis is not sensitive enough to estimate any but large amounts of yeast. If, however, tubes with a bulb at the end are used, the volume is increased and smaller concentrations can be conveniently estimated. Three tubes were used which had capacities given in table I.

Table I.

Tube.	Volume.	Equivalent of 1 scale division.
1	0·011 c.c.	$44·5 \times 10^6$ cells per c.c.
2	0·064 ,,	$7·65 \times 10^6$,, ,,
3	0·447 ,,	$1·11 \times 10^6$,, ,,

A suspension of yeast containing 216×10^6 cells per c.c. by counting under the microscope gave by centrifuging in tube 2 a deposit showing 27·7, 27·6, 27·5 scale divisions (0·5 mm. in length), on diluting to twice the volume the deposit was 14·1, 14·2, 13·9, and on diluting again to twice the volume the readings were 7·0, 7·4, 7·1. The averages are 27·6, $\frac{1}{2} \times 28·2$, $\frac{1}{4} \times 28·8$. One scale division on tube 2 is therefore equivalent to $216 \times 10^6/28·2 = 7·65 \times 10^6$ cells per c.c. The other tubes were similarly calibrated and checked one against the other. As tube 1 is a straight capilliary tube the yeast when it has settled down to a constant volume has a consistency of 4450 million per c.c. This corresponds approximately with the consistency of pressed barm. Yeast cells vary in size, but the figures given in table I have been used throughout the paper to convert scale divisions into cells per c.c.

Carlson used a method of this kind, the deposit from about 15 c.c. being determined. Paine (*Proc. Roy. Soc.*, 1911, [*B*], **84**, 289) also employed straight capillary tubes for estimating the volume of yeast cells suspended in a liquid.

When the number of yeast cells is below a few million per c.c., yeast counts under the microscope were made to determine the concentration. The usual hæmacytometer was employed, but the average number of cells appearing per field was estimated and the concentration obtained by dividing this average by the volume of liquid appearing in the field of the microscope.

Methods of Growing the Yeast.

The medium used in most of these experiments was lightly hopped malt wort. Yeast grows readily in this medium and large crops are produced. To eliminate the influence of carbon dioxide small quantities of wort were placed in large test-tubes to which had been sealed a piece of glass tubing. The tube is then exhausted or filled with any desired gas, sealed up, and rotated in a thermostat. Most of the carbon dioxide passes from the liquid into the space above. In some experiments accumulation of carbon dioxide is required. The fermentations were then carried out in straight tubes in which the liquid is sealed. High pressures of gas are obtained in this way. The yeast used in most cases was a Burton yeast (*S. cerevisiae*). In some experiments a pure culture of actively growing yeast was used, and in others quiescent yeast (pressed barm).

The Influence of Seeding on the Crop.

Tests were first made to determine whether large seedings of yeast would grow. The results, which are summarised in table II (p. 123), show what conditions must be fulfilled for growth to take place.

If actively growing yeast cells are used for seeding, normal growth takes place even though the seeding is very large (370×10^6 cells per c.c.). Large seedings of quiescent yeast cells show only a small growth (Expt. *h*). When the carbon dioxide cannot escape, moderately large seedings show no growth at all (Expt. *i*).

Under conditions of continual agitation larger crops were obtained, and the cell increase was found to be approximately constant, although the seeding varied greatly. In the following experiments about 3 c.c. of wort (D 1·050) were placed in a tube of capacity about 100 c.c., the tube being afterwards exhausted and sealed. The time of growth was three days at 20°.

TABLE II.

Wort, D 1·050. *Yeast concentrations, unit* $= 7 \cdot 65 \times 10^6$ *cells per c.c.*

Expt.	Temp.	Time.	Yeast.	Vessel.	Agitation.	Seeding.	Crop.	Cell increase.
a	25°	2 days	actively growing	large tubes exhausted	occasional shaking	49·3	62·5	13·2
b	25	2 ,,	,,	,,	,,	37·0	48·7	11·7
c	25	2 ,,	,,	,,	,,	24·7	37·0	13·7
d	25	3 hours	,,	flask	,,	25·2	32·5	7·3
e	25	1 day	,,	,,	,,	25·2	37·2	12·0
f	25	3 hours	quiescent	,,	,,	15·0	19·1	4·1
g	25	1 day	,,	,,	,,	15·0	28·0	13·0
h	25	1 ,,	,,	,,	,,	33·1	35·2	2·1
i	15	1 ,,	,,	sealed tube almost full	,,	18·1	18·1	0·0

TABLE III.

Yeast concentrations, unit = $7{\cdot}65 \times 10^6$ *cells per c.c.*

Expt.	Seeding.	Crop.	Cell increase.	Average.
a	37·1	56·0	18·9	18·8 = 143 × 10^6 cells per c.c.
	27·8	48·6	20·8	
	18·6	37·9	19·3	
	13·9	30·6	16·7	
	9·3	25·9	16·6	
	4·6	25·1	20·5	
b	19·3	37·8	18·5	17·2 = 132 × 10^6 cells per c.c.
	13·6	29·7	16·1	
	3·4	20·4	17·0	

The Influence of Carbon Dioxide on the Crop.

A wort (D 1·050) was seeded with yeast. A tube was filled almost completely, exhausted to remove dissolved air, and then sealed. Into a large tube was introduced a small quantity of the seeded wort, and this tube was exhausted and sealed. Both were rotated slowly at 20°. The yeast increase in the first case amounted to 30×10^6 cells per c.c., and in the second to 140×10^6 cells per c.c. This great difference is attributed to the carbon dioxide which remains in solution in the first case, and is removed in the second. If simultaneously an ordinary fermentation open to the atmosphere is carried out, the cell increase amounts to about 80×10^6 cells per c.c. This is a typical result obtained from a large number of experiments of this kind. It was considered probable that carbon dioxide could be made the limiting factor which determines the growth. The matter was tested by varying the exhausted space above the wort and determining the influence such variations had on the crop. If v_1 and v_2 are the volumes of liquid and space respectively, then the concentration of carbon dioxide in the liquid when a given amount of gas is formed is proportional to $\alpha = \frac{v_1 + v_2/s}{v_1}$, where s is coefficient of absorption of the gas in the liquid. A consideration of Fig. 1 shows that the cell increase should be proportional to α if the carbon dioxide is the limiting factor. This was found to be the case, as table IV (p. 125) shows.

If the tube is full ($\alpha = 1$) cell increase is $2{\cdot}9 = 22 \times 10^6$ cells per c.c. In Expt. *g*, where the space above is great, proportionality no longer exists. When more dilute worts were used, similar results were obtained, but as the space increased the deviation from proportionality occurred earlier. Experiments in which the space above was not exhausted, but filled with air, showed that the air

TABLE IV.

Wort, D 1·101. *Small seeding of yeast; exhausted tubes; temp.* = 25°; *tubes rotated three days*; $s = 0{\cdot}70$.

Expt.	v_1.	v_2.	a.	Crop (unit = $7{\cdot}65 \times 10^6$ cells per c.c.).	Crop/a.
a	23·3	1·2	1·08	3·0	2·8
b	23·0	1·3	1·08	3·0	2·8
c	14·5	4·8	1·46	4·1	2·8
d	11·8	4·0	1·48	4·5	3·1
e	10·3	8·3	2·13	6·1	2·9
f	12·3	11·7	2·33	6·5	2·8
g	7·4	17·2	4·26	9·9	2·3
				Average (excluding *g*) ...	2·9

increased the crop. One c.c. of air ($\frac{1}{5}$ c.c. oxygen) caused an increased growth averaging 15×10^6 cells.

The Influence of Air and Oxygen on Growth and Crop.

Small seedings of yeast in wort were allowed to grow one to two days at 20° in tubes which were continually rotated. Some of the tubes were exhausted, some filled with air, oxygen, and carbon dioxide. The constants of growth were calculated in the usual way, and the results are summarised in table V.

TABLE V.

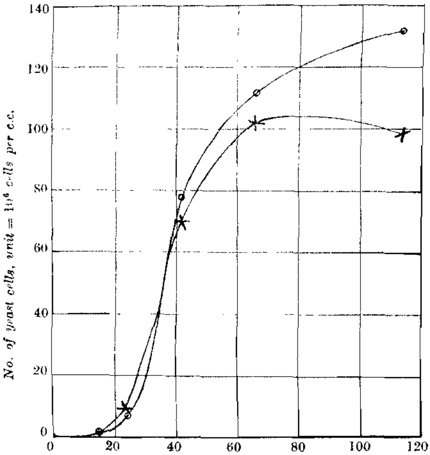
	Wort, D 1·047.		Wort, D 1·040.	
	0·434*K*.	G.T.	0·434*K*.	G.T.
Exhausted	0·110	2·7 hours.	0·109	2·7 hours.
Air	0·107	2·8 ,,	0·092	3·3 ,,
60 per cent. oxygen + 40 per cent. nitrogen	0·096	3·1 ,,	—	—
100 per cent. oxygen	0·085	3·5 ,,	—	—
100 per cent. carbon dioxide	0·079	3·8 ,,	0·073	4·1 hours.

The influence of air on the whole range of growth was then investigated, large tubes being used to eliminate the influence of carbon dioxide. The curves in Fig. 2 show the retarding influence of air during the early stages of growth and the favouring effect during the latter stages. The final yeast crop is greater under aerobic conditions.

In tables VI and VII are summarised some experiments on yeast growth in worts saturated with air. Wort (D 1·040) was introduced into a pressure flask and seeded with yeast. All dissolved air was rapidly removed by exhausting the flask. Fifty c.c. of the seeded wort were then introduced into a large test-tube. A

parallel experiment was made with wort saturated with air. Although in the first case the wort is exposed to the atmosphere and traces of air become dissolved, the amount dissolved in the second case is much greater and the effect on growth is very noticeable.

Fig. 2.



Time of growth in hours.
Anaerobic growth ×.
Aerobic growth ○.
Influence of CO_2 *eliminated.*

Table VI.

Temp. about 15°. *Unit* = $7 \cdot 65 \times 10^6$ *cells per c.c.*

Yeast.	Seeding.	Time of growth.	Cell increase: Exhausted wort.	Cell increase: Aerated wort.	Ratio.
Quiescent	1·4	18 hours.	1·7	2·5	**100 : 148**
,, ...	1·4	24 ,,	1·5	3·4	**100 : 227**
,, ...	3·0	48 ,,	5·0	7·3	**100 : 146**
,, ...	3·0	18 ,,	2·8	4·0	**100 : 143**
Actively growing	0·2	48 ,,	2·3	5·5	**100 : 239**
,,	0·1	48 ,,	2·0	4·0	**100 : 200**

The experiment was repeated, but the wort, both free from air and saturated with air, was placed in bottles. The bottles were filled completely with the liquid and stoppered to prevent escape of gas. In this case no such differences were observed.

TABLE VII.

Temp. about 15°. *Unit* $= 7{\cdot}65 \times 10^6$ *cells per c.c.*

Yeast.	Seeding.	Time of growth.	Cell increase: Exhausted wort.	Cell increase: Aerated wort.	Ratio.
Quiescent	1·0	18 hours.	1·8	1·8	100 : 100
,, ...	1·0	18 ,,	1·1	1·1	100 : 100
Actively growing	1·5	18 ,,	2·8	3·0	100 : 107
,,	0·2	40 ,,	2·5	2·8	100 : 111
,,	0·2	48 ,,	2·6	2·8	100 : 108

A number of experiments were then made in which yeast growth took place under anaerobic conditions and under conditions that a limited quantity of air was present. The tubes were rotated in a thermostat. Usually these small quantities of air had little or no influence on the yeast growth. In Expt. *e*, when large quantities of air are present, an appreciable retardation in growth is noticed.

TABLE VIII.

Temp. 20°. *Unit* $= 7{\cdot}65 \times 10^6$ *cells per c.c.*

Expt.	Yeast.	Vol. liquid : vol. air.	Seeding.	Time of growth.	Cell increase: Anaerobic	Cell increase: aerobic.	Ratio.
a	Quiescent	5 : 1	0·2	48 hours.	4·7	4·8	100 : 102
b	,,	1 : 1	5·2	2 ,,	1·4	1·3	100 : 93
c	,,	1 : 1	5·2	6 ,,	5·7	5·1	100 : 90
d	,,	5 : 150	2·9	4½ ,,	1·1	1·0	100 : 90
e	,,	5 : 150	2·9	6 ,,	2·3	1·6	100 : 70
f	Actively growing.	1 : 1	1·7	8 ,,	5·7	6·4	100 : 113

All these experiments show that small quantities of air have little influence so long as the concentration of the carbon dioxide is controlled. The results are in accordance with the idea that dissolved air aids yeast growth owing to the effect it has in lessening the supersaturation of the wort with carbon dioxide. The early stages of growth of quiescent yeast do not require air (table VIII, Expts. *a*, *b*, *c*, *d*). The following experiments were carried out to test H. T. Brown's suggestion that oxygen absorbed by the seeding yeast determines the subsequent growth. Yeast was grown in a small quantity of wort in an exhausted tube *A*. This yeast was

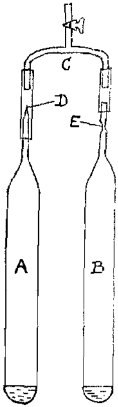
used to seed fresh wort in another tube, the process being carried out under strictly anaerobic conditions in the manner shown in Fig. 3. The T-piece *C* is exhausted and the wort in *B* is boiled to free it from air. The point *D* is then broken off, some of the

TABLE IX.

Expt.	Density of wort.	Time of growth and temp.	Crop (unit=$7 \cdot 65 \times 10^6$ cells per c.c.).
1	1·040	2 days at 25°	8·0
2	1·052	„ 20	10·0
3	1·063	„ 20	15·1
3*a*.........	1·063	„ 20	15·0
4	1·040	„ 20	11·4
4*a*.........	1·040	„ 20	11·2

liquid from *A* passes into *B*, which is then sealed at *E*. The results which are given in the above table show that good crops were obtained in tube *B* in spite of all absence of air.

FIG. 3.



In Expts. 3*a* and 4*a* the seeded wort was allowed to come in contact with the air for some hours and the tube then exhausted. This contact with the air had, however, no influence on the subsequent crop. There seems therefore no necessity for oxygen to be at the disposal of the yeast used for seeding.

The Influence of Concentrations of Sugar.

Some difficulty was experienced in obtaining a suitable medium to show the effect of sugar on yeast crops when this constituent of the medium is made the limiting factor. The medium finally chosen was the residue of a fermented wort (D 1·080). This wort was fermented with yeast and the alcohol distilled off. The process was repeated in order to free the medium entirely from fermentable sugar. To the final residue (D 1·017) was added small amounts of glucose, and this proved a good medium for wild yeast growth, although unsuitable for the growth of *S. cerevisiae*. The following table summarises measurements of *K*, *F* and crops with different concentrations of sugar, the organism used being a wild yeast of the *S. ellipsoideus* type.

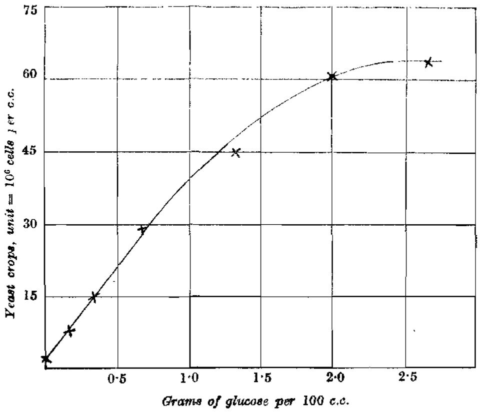
TABLE X.

Temp. = 20°. K = constant of growth in hours^{-1}.
F = grams of sugar fermented per hour per yeast cell.
K/F = yeast cells produced per gram fermented.

Grams of glucose per 100 c.c.	G.T.	K.	F.	K/F.
1·50	2·86 hours.	0·242	57×10^{-12}	4200×10^6
1·00	2·84 ,,	0·244	57	4300
0·50	2·84 ,,	0·244	56	4400
0·20	2·82 ,,	0·246	53	4600
			Average ...	4400×10^6

According to table X, when 1 gram of sugar is fermented, 4400×10^6 cells should be produced. Some rather indefinite cor-

FIG. 4.



rection has to be made for the amount of sugar used in building up the yeast. This correction would reduce the figure to approximately 3700×10^6. The curve, Fig. 4, shows proportionality between crop and initial glucose concentration up to about 1 per cent. of sugar. The slope of the curve corresponds with

3900×10^6 cells per gram, a figure in fair agreement with that calculated from K and F.

Influence on Temperature.

The following table summarises measurements of K and F of yeast (*S. cerevisiae*) in wort (D 1·040). The ratio K/F is approximately independent of temperature.

TABLE XI.

Temp.	G.T.	K.	F.	K/F.
10°	11·6 hours.	0·060	$12{\cdot}5 \times 10^{-12}$	4800×10^6
15	6·4 ,,	0·108	24·5	4400
20	2·95 ,,	0·235	47·0	5000
25	1·77 ,,	0·392	75·0	5200
			Average ...	4900×10^6

4900×10^6 cells are therefore produced when 1 gram of sugar is fermented. Assuming that this amount of yeast uses up 0·2 gram of sugar for its growth, 1·2 grams of sugar produce 4900×10^6 yeast cells (about 1·2 grams of pressed yeast). This represents the maximum possible crop.

In table XII is given the actual crops obtained at 15° and 25° under conditions that the sugar is the limiting factor (a and b), and under conditions that the carbon dioxide is the limiting factor (c and d). The medium in (a) and (b) is a mixture of 50 c.c. fermented wort residue and 5 c.c. of wort (D 1·040), and the experiment is carried out in large exhausted tubes. In (c) and (d) wort (D 1·101) is used in long tubes, half-filled in (c) and two-thirds filled in (d). They were exhausted and sealed. The cell increase was almost the same at 15° and 25°.

TABLE XII.

Unit $= 7{\cdot}65 \times 10^6$ *cells per c.c.*

	Seeding (actively growing).	15°		25°	
		Cell increase.	Time of growth.	Cell increase.	Time of growth.
a	4·8	2·3	2 days	2·3	1 day
b	0·7	2·2	2 ,,	2·5	1 ,,
c	1·8	7·1	2 ,,	7·1	1 ,,
d	0·5	3·4	3 ,,	3·8	2 ,,

Growth of Yeast in Malt Wort.

As a result of these experiments it is suggested that the generally accepted views on yeast growth should be considerably modified.

The influence of carbon dioxide is greater than has been realised, and great variations in the crop are obtained by altering the concentration of the carbon dioxide in the wort. Air (oxygen) has much less influence than is usually attributed to it. It plays no part in the initial budding of the yeast (the lag phase in growth) and has no direct accelerating influence during the first stages of growth. Later stages are favourable influenced by air; the aerobic vegetative growth here comes into consideration. Air dissolved in wort favours yeast growth. This is considered to be due to a decrease in the supersaturation of the wort with carbon dioxide and not to the yeast cell requiring free oxygen for its development.

Note on Spore Formation of Yeast Cells.

Little is known of the chemical reactions which accompany the formation of spores in yeast cells, but the belief is very generally held that oxygen plays an essential part in the process. This belief seems justified, but it was found that traces of air are sufficient to induce sporulation. The experiments were carried out in the following manner. Young and vigorous yeast cells of a wild yeast which readily formed spores were mixed with slightly acidified water (0·2 per cent. phosphoric acid neutralised with potassium hydroxide to give a P_H value 5—6) so that the solution was just turbid. Some of the liquid was placed in sterile conical flasks and some in tubes, which were then carefully exhausted. In two days at 23° abundant spore formation took place in the flasks, whilst no spores were formed under anaerobic conditions. In some cases a small quantity of air was allowed to enter the exhausted tube. One cm. pressure of air in the tube was found to cause the production of spores.

It is sometimes stated that the growth of yeast spores requires air. This proved incorrect, for spores were found to develop readily in wort free from air.

Burton-on-Trent.

[*Received, December 9th*, 1920.]

XV.—*The Volumetric Estimation of Mixtures of Acids and of Bases, and of Polybasic Acids or Bases.*

By Henry Thomas Tizard and Alfred Reginald Boeree.

The conditions which control the accuracy of titration of mixture of acids or bases have hitherto been too much obscured by somewhat complicated mathematical expressions to allow of their ready application to particular cases. The object of the present pape is to point out and illustrate certain relations which are applicabl in all but very exceptional circumstances.

The estimation of bi- and ter-valent acids or bases in solution i a special case of the estimation of mixtures of acids or bases. I an aqueous solution contains one equivalent of a weak acid HA_1 and x equivalents of a weak acid HA_2, the dissociation constant of which are K_1 and K_2 respectively (K_1 being $>K_2$), the conce tration of hydrions in the solution after the addition of on *equivalent of a strong base BOH* can be calculated in th following way:

Suppose the solution is sufficiently dilute for the assumption t be made that for all practical purposes the dissociation of an salt present is complete. Then there is present in V litres solution one equivalent of the ion **B**; y equivalents of A'_1, sa and therefore $1-y$ equivalents of A'_2, C_H being negligible.

Hence, since

$$K_1C_{HA_1} = C_H \times C_{A_1}$$

and

$$K_2C_{HA_2} = C_H \times C_{A_2},$$

we have

$$K_1\frac{1-y}{V} = C_H \times \frac{y}{V}$$

$$K_2\frac{x-(1-y)}{V} = C_H \times \frac{1-y}{V}$$

or

$$C_H^2 = K_1K_2\frac{x-(1-y)}{y} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In the special case when $x=1$, we have

$$C_H = \sqrt{K_1K_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and C_H is independent of dilution within wide limits. Hence, order to titrate a dibasic acid, or a mixture of acids in equivale

proportions, to the half-way point, an indicator must be chosen which changes over at concentration of hydrions given by equation (2). This condition is already well known.

Now the accuracy of the titration is affected not only by the choice of the indicator, but also by the effect on the acidity of the solution of small changes in the amount of alkali added near the "equivalent" point. To calculate this, suppose $(1+z)$ equivalents of BOH are added to a solution containing one equivalent each of HA_1 and HA_2. Then if y equivalents of A'_1 are present in the solution, there are $(1+z-y)$ of A'_2, and therefore,

$$K_1(1-y)=C_H \times y,$$
$$K_2(y-z)=C_H \times (1+z-y),$$

or

$$\frac{C_H^2}{K_1K_2}=\frac{(1-y)(y-z)}{y(1+z-y)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and

$$\frac{K_1}{K_2}=\frac{y(y-z)}{(1-y)(1+z-y)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In order to get a sharp end-point, it is necessary that a small excess or deficit of alkali should produce a large change in the concentration of hydrions. Inspection of the expression on the right-hand side of equation (3) shows that the nearer y is to unity, the smaller will be the value of the expression for small values of z. Trial shows that if C_H is to be equal to $\frac{1}{2}\sqrt{K_1K_2}$ when $z=0{\cdot}01$, or, in other words, if the concentration of hydrions at the equivalent point is to be halved by adding as 1 per cent. excess of alkali, then $y=0{\cdot}997$ approximately. Substituting this in (4), we see that K_1/K_2 in this case must be of the order of 10^4. *The larger the ratio of K_1 to K_2, the sharper is the end-point*, and all necessary information can be obtained by giving K_1/K_2 certain arbitrary values, then calculating y from equation (4) for different values of z, and finally substituting these figures in equation (3), thus obtaining the corresponding value of $\frac{C_H}{\sqrt{K_1K_2}}$.

The following tables give calculations for various values of K_1/K_2 and for various additions of alkali. It is assumed for the sake of clearness that 20 c.c. of a solution containing equivalent quantities of the two acids are titrated by an equivalent solution of a strong base.

TABLE I.

C.c. of base added.	Approximate values of $\frac{C_H}{\sqrt{K_1K_2}}$ when $\frac{K_1}{K_2}$ = 10².	10³.	10⁴.	10⁵.	10⁶.
8·0	3·0	8·0	25·0	80·0	250·0
9·0	1·8	4·0	11·0	35·0	110·0
9·5	1·4	2·1	5·5	17·0	56·0
9·7	1·2	1·6	3·6	10·0	32·0
9·8	1·1	1·4	2·5	6·8	20·0
9·9	1·05	1·2	1·6	3·5	10·0
10·0	1·0	1·0	1·0	1·0	1·0
10·1	0·95	0·83	0·63	0·29	0·1
10·2	0·9	0·71	0·4	0·16	0·05
10·3	0·83	0·63	0·28	0·10	0·031
10·5	0·71	0·48	0·18	0·06	0·018
11·0	*0·56*	*0·25*	*0·09*	*0·028*	*0·009*
12·0	0·33	0·12	0·04	0·012	0·004

It is clear from these figures that when K_1/K_2 is very large, 10^6, say, a small excess or deficit of alkali near the equivalent point makes a very large difference to the hydrion concentration; a 1 per cent. error alters the conceutration by a factor of 10. Hence not only will the end-point be very sharp, but it is not necessary to be too particular about the choice of an indicator, so long as the end-point of the indicator is somewhere between $10\sqrt{K_1K_2}$ and $1/10\sqrt{K_1K_2}$.

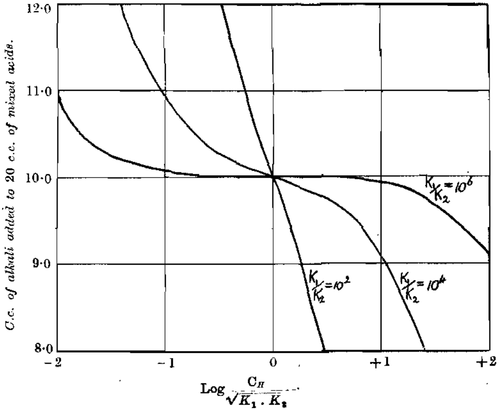
If $K_1/K_2=10^2$, a 1 per cent. excess or deficit of alkali alters the hydrion concentration only by 5 per cent.; it requires more than a 10 per cent. excess or deficit before the hydrion concentration is altered by a factor of 2. It is hardly possible, even with the best indicators, to be certain of titrating by eye to within a factor of 2, unless elaborate precautions are taken, so that if $K_1/K_2=10^2$, titration will be uncertain and inaccurate even if an indicator is chosen which changes over very nearly at the correct hydrion concentration given by $C_H=\sqrt{K_1K_2}$.

These conditions are illustrated in the figure. The theoretical half-way point is supposed to correspond with an addition of 10 c.c. of the alkaline solution. The logarithm of $\frac{C_H}{\sqrt{K_1K_2}}$ is plotted against the amount of alkali added, and the flatness of the curves near the equivalent point gives a measure of the accuracy obtainable. A factor of 2 in the hydrion concentration corresponds with a difference of 0·3 in the logarithm, that is, 3 units on the scale of abscissæ. Using this criterion, it is clear that even if K_1/K_2 is as great as 10^4, an accuracy of 1 per cent. can only be obtained if an indicator is chosen which changes over as near as possible

to the true equivalent point; although if such an indicator is not available, the curves can be used to correct approximately the results obtained by the use of the best available indicator.

In general, consideration of the figures of table I shows that an accuracy of 1 per cent. in the titration of a dibasic acid in the half-way point by ordinary methods cannot be trusted, unless the ratio K_1/K_2 is at least equal to 10^4. This condition can be obtained directly, and more accurately, from equations (3) and (4).

If the concentration of hydrions at the equivalent point is halved by a 1 per cent. excess of alkali, it has already been shown



that $y = 0{\cdot}997$. Substituting $y = 0{\cdot}997$ and $z = 0{\cdot}01$ in equation (4), we get

$$\frac{K_1}{K_2} = 2{\cdot}5 \times 10^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Similarly, if the same alteration in C_H is caused by an excess of alkali of 0·1 per cent., or one part in a thousand, then we must have

$$\frac{K_1}{K_2} = 2{\cdot}5 \times 10^6 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The same relations hold good, of course, for the estimation of

mixtures of bases, except that at the equivalent (half-way) point, we have

$$C_{OH} = \sqrt{K_1K_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and ∴

$$C_H = \frac{K_w}{C_{OH}} = \frac{K_w}{\sqrt{K_1K_2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where K_w is the dissociation constant of water, and K_1, K_2 the dissociation constants of the bases.

Before giving the results of experiments made to check these conclusions, it will be useful to generalise these conditions, and to apply the general conditions to other special cases of interest.

The special case we have already discussed is that where $x=1$. Now when x is not unity, that is, when the acids are mixed in any proportions, it is still true to say that for accurate titration of the strongest acid in solution, y must be very nearly equal to 1, when an equivalent amount of alkali has been added. Hence from equation (1) we get

C_H, *or in the case of* bases C_{OH}, at the *equivalent point* =

$$\sqrt{xK_1K_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and by exactly the same methods as given above, we find that the condition of titration to 1 per cent. is that

$$\frac{K_1}{xK_2} \text{ shall be at least} = 2{\cdot}5 \times 10^4 \quad . \quad . \quad . \quad . \quad (10)$$

and the condition for titration to 0·1 per cent. is that

$$\frac{K_1}{xK_2} > 2{\cdot}5 \times 10^6 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

These general conditions can be applied in nearly every case; i is only when solutions are so concentrated that the "neutral salt' effect comes in that they are likely to fail. The titration of a single acid or base *in the presence of water is simply a specia case, where the second dissociation constant* K_2 is equal to $K_w \times V$ where V is the dilution, and K_w the so-called dissociation constan of water. At 18°, $K_w = 0{\cdot}6 \times 10^{-14}$, so that if $V=20$, $K_w \times V$ i approximately 10^{-13}. The choice of an indicator in solutions o approximately this strength is therefore given by

$$C_H = \sqrt{K_1 \times 10^{-13}} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

and the condition of titration to 1 per cent. is approximately

$$\frac{K_1}{10^{-13}} = 2{\cdot}5 \times 10^4 \text{ or } K_1 = 2{\cdot}5 \times 10^9 \quad . \quad . \quad . \quad . \quad (13)$$

The absence of a suitable indicator may upset this condition; i is only when K_1 is much larger that considerable latitude in th choice of an indicator is possible.

The following experiments illustrate the theory given above:

(1) (*a*) The dissociation constant of ammonia is about $1{\cdot}8 \times 10^{-5}$. Hence the concentration of hydroxyl ions in the solution when equivalent quantities of $N/10$-ammonia and $N/10$-hydrochloric acid are mixed is

$$C_{OH} = \sqrt{1{\cdot}8 \times 10^{-5} \times 10^{-13}}$$
$$= 1{\cdot}3 \times 10^{-9} \text{ approximately}$$
$$C_H = \frac{K_w}{C_{OH}} = \frac{0{\cdot}6 \times 10^{-14}}{1{\cdot}3 \times 10^{-9}} = \text{about } 5 \times 10^{-6}.$$

Methyl-red changes over at this concentration, and this indicator is known to be very good for the estimation of ammonia. Further, since (see equation 13) $\frac{1{\cdot}8 \times 10^{-5}}{10^{-13}} = 1{\cdot}8 \times 10^{8}$, that is, is much greater that 10^4, a considerable latitude in the choice of an indicator is permissible. For example, both methyl-orange (C_H = about 10^{-4}) and cresol-red (C_H = about 5×10^{-8}) are reasonably good indicators for ammonia, although not so accurate as methyl-red.

An approximately $N/10$-solution of ammonia titrated by $N/10$-hydrochloric acid gave the following results:

Indicator: methyl-red. Acid added.	25 C.c. of ammonia taken. Colour of indicator.	*Indicator*: cresol-red. Acid added.	25 C.c. of ammonia taken. Colour of indicator.
24·0 c.c.	yellow	22·5 c.c.	pink
24·65	„	24·1	orange-pink
24·7	orange	**24·6**	dull yellow
24·8	pink	25·0	very yellow

The correct end-point is very nearly 24·7; titration when using cresol-red is much less certain.

(*b*) Now consider the conditions if it is required to estimate ammonia in presence of an approximately equivalent quantity of aniline. Aniline is a very weak base, with a dissociation constant of about $3{\cdot}5 \times 10^{-10}$. Hence the concentration of hydroxyl ions in the solution when an amount of acid equivalent to the ammonia present is added (the half-way point) is:—

$$C_{OH} = \sqrt{1{\cdot}8 \times 10^{-5} \times 3{\cdot}5 \times 10^{-10}} \text{ (see equation 7)}$$
$$= 8 \times 10^{-8}$$

or

$$C_H = \frac{0{\cdot}6 \times 10^{-14}}{8 \times 10^{-8}} = 7 \times 10^{-8}.$$

Further, since the ratio $\frac{K_1}{K_2} = \frac{1{\cdot}8 \times 10^{-5}}{3{\cdot}5 \times 10^{-10}} = 5 \times 10^{-4}$, it is necessary to be particular over the choice of an indicator in order to get a result within 1 per cent. Methyl-red will therefore be

quite unsuitable, whereas cresol-red may be expected to give a good result.

Twenty-five c.c of the same solution of ammonia were mixed with 25 c.c. of an approximately $N/10$-solution of aniline and *titrated against $N/10$-hydrochloric acid.*

Indicator : methyl-red.

C.c. of acid added.	Colour of indicator.
24·1	greenish-yellow
26·8	faint change
28·3	yellowish-orange
29·6	pinkish-orange
33·0	pink

Note the indefiniteness and inaccuracy of the end-point, which *should have occurred at 24·7 (see above).*

Indicator : cresol-red.

C.c. of acid added.	Colour of indicator.
24·0	orange-pink
24·3	still slightly pink
24·55	orange
24·6	dull yellow
24·7	quite yellow

Note the sharp end-point, correct to within 1 per cent. This is a very good example of the substantial accuracy of the conditions given by theory; it is interesting to note the striking effect caused by the presence of so weak a base as aniline in a solution of ammonia.

(2) Consider next the estimation of mixtures of bases of about the same strength as ammonia and β-picoline. Take first the estimation of such a base as picoline alone in aqueous solution, approximately $N/10$. Since the dissociation constant is 1×10^{-8}, we have

$$\frac{K_1}{\text{“}K_2\text{” (water)}} = \frac{10^{-8}}{10^{-13}} = 10^5 > 2{\cdot}5 \times 10^4.$$

Hence it should be possible to estimate β-picoline to within 1 per cent., but only by choosing the indicator with care. When an equivalent amount of hydrochloric acid is added

$$C_{OH} \text{ is approximately} = \sqrt{10^{-8} \times 10^{-13}} = 3 \times 10^{-11}$$

and $$C_H \quad ,, \qquad ,, \qquad = \frac{0{\cdot}6 \times 10^{-14}}{3 \times 10^{-11}} = 2 \times 10^{-4}.$$

The best indicator to use is therefore methyl-orange (orange to pink); methyl-red will be quite unsuitable.

Titration of an Approximately N/10-*Solution of β-Picoline by Hydrochloric Acid.*

C.c. of acid added.	Colour of indicator. Methyl-orange.	Methyl-red.
15·0	yellow	yellowish-orange
18·0	,,	pinkish-orange
19·0	,,	pink
22·5	,,	—
23·0	orange	—
23·4	pink	—

The end-point given by methyl-orange, namely, 23·0 c.c., is probably within 1 per cent. of the correct value; that given by methyl-red is hopelessly inaccurate.

In the case of a mixture of equivalent amounts of ammonia and β-picoline, the concentration of hydroxyl ions at the half-way point is

$$C_{OH} = \sqrt{1 \cdot 8 \times 10^{-5} \times 10^{-8}}$$
$$= \text{about } 4 \times 10^{-7},$$

or

$$C_H = \frac{0 \cdot 6 \times 10^{-14}}{4 \times 10^{-7}} = 1 \cdot 5 \times 10^{-8}.$$

Phenolphthalein (about 10^{-8}) should therefore indicate a fairly correct half-way point, but it can only be very approximate, since

$$\frac{K_1}{K_2} = \frac{1 \cdot 8 \times 10^{-5}}{10^{-3}} = 1 \cdot 8 \times 10^{-3},$$

which is considerably less than $2 \cdot 5 \times 10^{-4}$.

A mixture of 25 c.c. each of the standard ammonia solutions and of the above β-picoline solution gave the following results when titrated against N/10-hydrochloric acid:

C.c. of acid added.	Colour of indicator. Phenolphthalein.
20·8	pale pink
21·8	trace pink
22·0	colourless

The correct half-way point is 24·7 [see example (1)].

The titration was then completed by adding methyl-orange to the solution.

C.c. of acid added.	Colour of indicator (methyl-orange).
45·0	yellow
46·3	yellowish-orange
47·5	orange
48·0	pinkish-orange

The correct end-point should have been 24·7 + 23·0 = 47·7, which agrees as well as could be expected with that found.

(3) Similar experiments were made with mixtures of phenol and acetic acid. The dissociation constant of phenol is given as $1 \cdot 3 \times 10^{-10}$; it is therefore too weak an acid to be estimated volumetrically, for $\frac{1 \cdot 3 \times 10^{-10}}{10^{-13}} = 1 \cdot 3 \times 10^{3}$ is much smaller than $2 \cdot 5 \times 10^{4}$. K for acetic acid is $1 \cdot 8 \times 10^{-5}$; the correct indicator for its estimation alone is therefore given by

$$C_H = \sqrt{1 \cdot 8 \times 10^{-5} \times 1 \cdot 0 \times 10^{-13}}$$
$$= 1 \cdot 3 \times 10^{-9} \text{ approximately.}$$

Phenolphthalein (10^{-8}) is quite satisfactory, since the ratio $\frac{1 \cdot 8 \times 10^{-5}}{1 \cdot 0 \times 10^{-13}}$ is very large. If it is required to estimate the acetic acid present in a mixture of this with phenol in approximately equivalent proportion, an indicator must be used which changes over at

$$C_H = \sqrt{1 \cdot 8 \times 10^{-5} \times 1 \cdot 3 \times 10^{-10}}$$
$$= 5 \times 10^{-8}$$

Hence cresol-red should indicate the half-way point, whereas phenolphthalein will give too high results, for the ratio

$$\frac{1 \cdot 3 \times 10^{-10}}{1 \cdot 8 \times 10^{-5}} = 7 \times 10^{4}$$

is too low to allow of any latitude in the choice of an indicator.

Twenty-five c.c. of approximately $N/10$-acetic acid were found to be neutralised by 25·15 c.c. of $N/10$-sodium hydroxide, using phenolphthalein. The end-point was very sharp, and this result is probably accurate to 0·1 per cent. The results obtained by titrating a mixture of 25 c.c. of the same acetic acid solution and 25 c.c. of $N/10$-phenol against $N/10$-sodium hydroxide were as follows:

	Colour of indicator.	
C.c. of alkali added.	Cresol-red.	Phenolphthalein.
25·0	yellow	colourless
25·3	pinkish-orange	,,
25·5	pink	,,
25·8	dark pink	trace pink

The results are in good agreement with theory; an equally good if not slightly better, half-way point was obtained by using azolitmin as an indicator ($10^{-7 \cdot 1}$); this suggests that the dissociation constant of phenol given in the literature is slightly too low.

(5) Some other examples may now be given in less detail. Monochloroacetic acid ($K = 1 \cdot 55 \times 10^{-3}$) cannot be estimated accurately in the presence of acetic acid ($1 \cdot 8 \times 10^{-5}$), since the rat

f the constants is too small. The total acid present can, of course, e accurately estimated by using phenolphthalein. The nearest ndicator for the "half-way" point would be that changing ver at

$$C_H = \sqrt{1{\cdot}55 \times 10^{-3} \times 1{\cdot}8 \times 10^{-5}} = 1{\cdot}7 \times 10^{-4}.$$

An attempt made to estimate the monochloroacetic acid in a iixture with an exactly equivalent quantity of acetic acid gave a esult, with methyl-orange, corresponding with 13·5±0·5 c.c. of tandard alkali, whereas the total acid present was neutralised by 5·75 *c.c. of alkali.*

On the other hand, trichloroacetic acid (3×10^{-1}) can be pproximately estimated in the presence of acetic acid, since the atio $\frac{3 \times 10^{-1}}{1{\cdot}8 \times 10^{-5}}$ is only slightly less than $2{\cdot}5 \times 10^4$. The best idicator to use is methyl-violet. Trial gave 12·8±0·2 c.c. for the alf-way point, and 25·70 c.c. for the end-point (phenolphthalein). he first and second steps of the "neutralisation" of phosphoric cid can, as is well known, be detected accurately by the use of iitable indicators. This agrees well with theory, for

$$K_1 = 1 \times 10^{-2},$$

$_2 = 2 \times 10^{-7}$, $K_3 = 4 \times 10^{-13}$, and the ratios $\frac{K_1}{K_2}$ and $\frac{K_2}{K_3}$ are large. he best indicator to use for the first step is that changing over ; $\sqrt{2 \times 10^{-9}} = 10^{-4{\cdot}35}$, that is, methyl-orange (orange to yellow); milarly, phenolphthalein is suitable for the second stage. The iird dissociation is too weak for a final "end-point" to be otained. These facts are, of course, well known, and are only ioted to show how they agree with the conditions given above.

Succinic acid ($K_1 = 6{\cdot}5 \times 10^{-5}$, $K_2 = 3 \times 10^{-6}$) cannot be titrated to half-way point, but maleic acid ($K_1 = 1{\cdot}3 \times 10^{-2}$, $K_2 = 3{\cdot}0 \times 10^{-7}$, tio $= 4 \times 10^4$) can, methyl-orange being a suitable indicator. As e second dissociation constants of these acids are fairly high, curate final "end-points" can be obtained in both cases by the e of phenol- or thymol-phthalein, so that titration to the half- iy point is unnecessary when the solution contains no other acid; it if another weak acid, for example, of the order of 10^{-7}, is esent in each solution, the succinic acid cannot be separately timated, but the maleic acid can by titrating to the half-way int with methyl-orange. This has also been confirmed by periment.

Finally, attention may be drawn to a point of some importance. lutions of acid salts are often recommended as "hydrion gulators." It should not be overlooked that if the salt is that

of a di- or tri-basic acid, the dissociation constants of which are very different, a small excess of base or acid in the solution will have a large effect. This is clearly shown by the figure on p. 135. For example, if a solution of disodium hydrogen phosphate is chosen *as the regulator, an excess of one part in a thousand of* sodium hydroxide or of phosphoric acid will alter the hydrion concentration nearly by a factor of 2, since

$$\frac{K_2}{K_3} = \frac{2 \times 10^{-7}}{4 \times 10^{-13}} = 0{\cdot}5 \times 10^6.$$

On the other hand, a similar excess in the case of sodium hydrogen succinate will have a negligible effect, since the ratio of the two dissociation constants of this acid is small. As stated in a previous paper (Tizard and Whiston, T., 1920, **117**, 151), it is considered that the best and most convenient way of preparing solutions of known hydrion content between $C_H = 10^{-3}$ and $C_H = 10^{-11}$ is by mixing solutions of ammonia and acetic acid, the relative strengths of which can be estimated with great accuracy.

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XVI.—*The Influence of the Solvent on the Temperature-coefficient of certain Reactions. A Test of the Radiation Hypothesis.*

By HENRY EDWARD COX.

IN a former paper (T., 1920, **117**, 493) the velocity of three analogous reactions—sodium naphthoxide and the alkyl iodides—in fifteen alcohols was discussed and a relation was shown between the constitution of the solvents and the effect on the velocity. The present paper deals with the temperature-coefficients of the reaction in different solvents of bromoacetophenone with aniline and of sodium naphthoxide with ethyl iodide.

The point of view adopted is that the reactions take place by the formation of intermediate compounds or solvent–solute complexes, the velocity being dependent on the constitution of the complex and hence on the constitution of the solvent. Much experimental evidence could be adduced in support of this, and the remark of Patterson and Montgomerie (T., 1912, **101**, 26), that solvents frequently affect different reactions in the same order, is capable of interpretation on this line. Further, it may be supposed that the

reaction—whether or not the solvent takes part in it—is brought about by the infra-red radiation present in the system as proposed by Lewis in his papers on catalysis.

A study of the temperature-coefficients in different solvents affords a crucial test whereby the radiation theory as developed by Lewis may be examined, and the results obtained in this investigation generally support the theory subject to certain restrictions on account of the special characters of the solvent.

It is now generally recognised that reaction velocity depends not on kinetic energy, but on the internal energy of the molecules concerned; they react when their energy exceeds a certain critical value. The well-known equation of Arrhenius, which agrees with the experimental data more nearly than any other of the many equations which have been proposed for the influence of temperature, involves the idea of a critical value for the energy of the molecule, although it was suggested that kinetic energy is principally concerned. Arrhenius applies van't Hoff's isochore to direct reactions by assuming an equilibrium between active and passive molecules, so that in the well-known equation $\log\frac{k_{t_1}}{k_{t_2}} = A\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$, A is a constant which denotes half the heat required to transform 1 gram-molecule from the passive to the active state.

Lamble and Lewis (T., 1914, **105**, 2330) deduce from this equation that when a positive catalyst is present in large quantity a diminution of the temperature-coefficient should follow. They state that (assuming the identity in nature of temperature and catalytic effects) when much catalyst is present the transformation from passive to active molecules should have taken place, and therefore temperature should have a less additional effect in accelerating the reaction. Arrhenius supposes, however, that the number of active molecules is so small that the concentration of the inactive molecules is, for purposes of calculation, equal to the concentration of the substance; so whilst Lamble and Lewis's statement may be correct in extreme cases it cannot apply to reactions where the velocity is accelerated only a relatively small number of times by the catalyst. In their experiments on the hydrolysis of methyl acetate, the acceleration by the added catalyst is only about forty times at constant temperature, and no regularity of effect on the temperature-coefficient is observed, which confirms the opinion that no diminution is required on the Arrhenius view. On the radiation theory such diminution is a necessary mathematical consequence, so that if a sufficient change of velocity can be examined experimentally, herein lies a test of this application of the quantum theory.

The fundamental equation for the influence of temperature on

the radiation theory is that of Marcelin and of Rice (*Compt. rend.*, 1914, **158**, 116, 407; and *Rep. Brit. Assoc.*, 1915, 397), namely, $\frac{d.\log k}{dt} = E/RT^2$, where R is the gas constant and E is the critical increment of internal energy which the molecule must receive before it can react. This equation leads to an integrated equation of the same form as that of Arrhenius; hence it is equally in accord with the experimental results. It has the merit also that E represents a definite physico-chemical property of the substances and which can be measured.

Lewis (T., 1916, **109**, 796), by suggesting that the increase in internal energy E which the molecule must receive before reacting is communicated to it by the infra-red radiation present in the system and absorbed in quanta of a definite frequency, correlates the velocity of reaction, effect of temperature, and added catalyst or solvent. Applying Planck's radiation formula to the Marcelin-Rice equation, Lewis draws the necessary conclusion that "any agency which increases the reaction velocity (positive catalysis) diminishes the temperature-coefficient of the constant; any agency which diminishes the velocity (negative catalysis) increases the value of the coefficient."

Skrabal (*Monatsh.*, 1916, **37**, 495), from an entirely different line of argument, arrives at a more general conclusion that the relations between reaction velocity, temperature effects, influence of the solvent, added catalyst, and photochemical action are all essentially the same; accordingly, change in the reaction velocity effected by any one of these factors diminishes as the magnitude of the velocity-constant rises. A special case of this generalisation is clearly that the temperature-coefficient will be inversely as the velocity in the presence of any given solvent or catalyst.

Experimental evidence either for or against these conclusions is up to the present rather scanty. Since the examples quoted by Lewis, a few more results have been published by Dhar (T., 1917, **101**, 707), who has obtained results from the investigation of certain reactions sensitive to light, in which there is a gradual diminution of the temperature-coefficient as the velocity rises, due to the increased concentration of the catalyst in aqueous solution. These experiments differ from those contemplated by the radiation hypothesis (ordinary thermal reactions) in being truly photochemical.

Apart from the question of the possible relations between the physical properties or chemical constitution of a solvent and its effect on the reaction velocity, it has been suggested that it may, for purposes of temperature-coefficients, be considered purely from the point of view of a catalyst; the experiments here described were

designed specially to test this application of the quantum theory in so far as it leads to a relation between velocity and temperature-coefficients. Two reactions have been measured in a range of solvents so selected as to obtain as wide a difference as possible in the velocities at one temperature and the value of the temperature-coefficient in each solvent has been found. If Lewis's deductions are correct there must be an inverse proportionality between velocity and temperature-coefficients.

One of the reactions measured is between molecules only, and is measured in a series of dissimilar solvents; the other is a dual reaction between ions and molecules jointly, and has been measured in a series of related solvents The object of this is to test the radiation hypothesis under widely differing conditions and to find in what respect its conclusions require modification on account of the special effects of a solvent, such as ionisation and the formation of definite complexes or intermediate compounds, which is indicated by the experimental results of so many papers to be found in the literature, and is supported by the conclusion deduced in the former paper that solvent action is in part a constitutive property of the solvent. The results will be discussed after the experimental data have been summarised.

EXPERIMENTAL.

The Velocity of the Reaction of ω-Bromoacetophenone with Aniline.

This reaction is a simple addition, no further change taking place in non-aqueous solution; this is shown by the analysis of the product. The bromoacetophenone was prepared by Rather and Reid's method (*J. Amer. Chem. Soc.*, 1919, **41**, 75), and recrystallised several times from hot alcohol. The aniline was redistilled and fractionated immediately before use (b. p. 183·5—184°). The requisite quantities were dissolved separately, so as to make the resulting solution $N/2$ with respect to each substance; a quantity of the solution was placed in each of six small tubes placed in the thermostat and the time counted from the moment of removing the first tube after allowing time for the tubes to attain the temperature of the bath. In methyl and ethyl alcohols, in which the reaction is very fast, the mixture was made in a small flask in the thermostat and a fraction withdrawn at intervals by a specially calibrated pipette. The reaction was followed by pouring the contents of the tube into cold water containing 5 c.c. of $N/10$-silver nitrate and some ferric sulphate acidified with nitric acid; the excess of silver nitrate was then titrated with $N/10$-thiocyanate. This gives a

measure of the concentration of the product containing the ionised halogen.

The temperatures for this reaction were 27·8°, 37·8°, and 47·8° registered on a standard thermometer. Time is reckoned in minutes, and the value of the velocity-constant obtained from the usual bimolecular equation; the results are calculated in terms of gram-molecules per litre. From the examples given below it will be seen that the results are concordant over the range of concentration investigated, and in certain of the solvents, in which after a time the salt produced begins to crystallise out, there appears no change in the velocity-constant. Duplicate experiments were made in several solvents, and the agreement is satisfactory.

The solvents used for this reaction were benzene, chloroform, nitrobenzene, acetone, and methyl, ethyl, *n*-butyl, and benzyl alcohols. These solvents were in each case carefully dehydrated and redistilled or fractionated, the same batch of solvent being used for each temperature, so that no variation in the temperature-coefficient could be due to a variation in the purity of the solvent. A few examples of the experimental data are as follows:

TABLE I.

Solvent: Chloroform.

Temperature, 27·8°.
1·646 c.c. titrations.

t.	KCNS/10.	$AgNO_3$/10.	*k.*
0°	4·92	4·92	—
68	4·65	4·92	0·000997
174	4·30	4·92	0·000937
263	3·99	4·92	0·000966
328	3·78	4·92	0·000981
	Mean	....	0·000970

Temperature, 47·8°.
1·646 c.c. titrations.

t.	KCNS/10.	$AgNO_3$/10.	*k.*
0°	4·92	4·92	—
65	4·20	4·92	0·00295
149	3·38	4·92	0·00309
270	2·66	4·92	0·00281
335	2·10	4·92	0·00311
	Mean	....	0·00299

Solvent: Methyl Alcohol.

Temperature, 27·8°.
1·646 c.c titrations.

t.	KCNS/10.	$AgNO_3$/10.	*k.*
0°	9·63	9·83	—
6	8·80	9·83	0·0404
11	8·34	9·63	0·0367
17	7·68	9·83	0·0400
21	7·42	9·83	0·0384
	Mean	....	0·0389

Temperature, 47·8°.
1·646 c.c. titrations.

t.	KCNS/10.	$AgNO_3$/10.	*k.*
0°	—	4·92	—
2	3·78	4·92	0·161
4	3·13	4·92	0·139
5	2·86	4·92	0·134
6	2·51	4·92	0·138
	Mean	....	0·143

TABLE I.—*continued.*

Solvent: Nitrobenzene.

Temperature, 37·8°.

1·646 c.c. titrations.

t.	KCNS/10.	$AgNO_3$/10.	*k.*
0°	4·92	4·92	—
15	4·14	4·92	0·0140
25	3·73	4·92	0·0136
42	3·06	4·92	0·0139
51	2·80	4·92	0·0136
	Mean		0·0135

Solvent: Acetone.

Temperature, 37·8°.

1·646 c.c. titrations.

t	KCNS/10.	$AgNO_3$/10.	*k.*
0°	—	4·92	—
11	3·89	4·92	0·0260
16	3·43	4·92	0·0277
24	2·97	4·92	0·0260
28	2·61	4·92	0·0279
	Mean		0·0269

The results of these and other experiments are summarised in table II.

TABLE *II.*

Solvent.	Temperature. 27·8°.	37·8°.	47·8°.
Ethyl ether	0·000607	—	—
Benzene	0·000644	0·000985	0·00150
Chloroform	0·000970	0·00186	0·00299
Nitrobenzene	0·00617	0·0135	0·0252
Acetone	0·0139	0·0269	0·00440
Benzyl alcohol	0·0208	0·0440	0·0924
n-Butyl ,, ...	0·0267	0·0550	0·116
Ethyl ,, ...	0·0290	0·0626	0·124
Methyl ,, ...	0·0389	0·0748	0·143

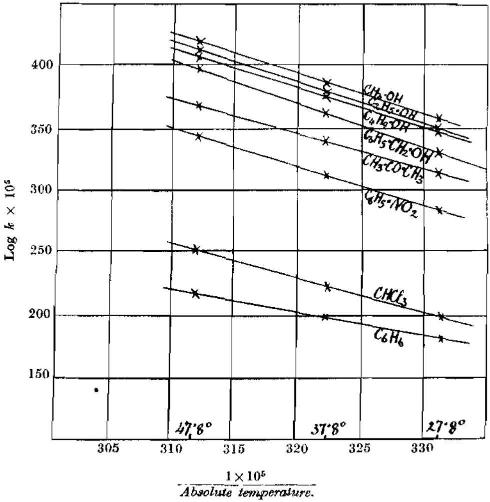
The velocity in methyl alcohol, which is the most rapid, is about seventy times that of the slowest of the series at the one temperature, and the other solvents examined give a good range of variation for the velocity-constant, so that if the temperature-coefficient is proportional to the velocity a distinct difference in its value is reasonably to be expected. Before proceeding to this point it is necessary to find whether the integrated equation of Arrhenius or of the radiation theory is in agreement with the experimental results. This may be conveniently tested graphically, for it is clear that if the logarithm of the velocity is plotted against the reciprocal of the absolute temperature, the results should lie upon a straight line if the equation is applicable. The slope of the line will indicate approximately the temperature-coefficient. The figure shows that these results are represented by the equation in question within the limits of experimental error.

Temperature-coefficients.

The most usual form of expressing temperature-coefficients is by the ratio $\frac{k_{t+10}}{k_t}$, the value of which for reactions at ordinary tem-

peratures is generally from 1·5 to 3·5 for thermal reactions, very large or very small values being usually associated with photochemical effects. It is, however, clear from the form of the equation $d \log k/dt = E/RT^2$ that the ratio for ten degrees varies inversely with the temperature, so that it is essential in comparing the temperature-coefficients for the reaction in all solvents that the same range of temperature be considered in all cases. The values of the

ω-Bromoacetophenone and aniline.



above ratio over the range 27·8° to 47·8° are shown in table III; it will be noted that the ratio $k_{37 \cdot 8°}/k_{27 \cdot 8°}$ is slightly higher than the ratio $k_{47 \cdot 8°}/k_{37 \cdot 8°}$, as is required by the theory.

The effect of temperature on the velocity is, however, better expressed, in terms of the radiation theory, by E, which represents the extra amount of energy in calories per gram-molecule which is required to enable the reaction to proceed. This constant is inde-

TABLE III.

Solvent	$\frac{k_{37\cdot8^\circ}}{k_{27\cdot8^\circ}}$	$\frac{k_{47\cdot8^\circ}}{k_{37\cdot8^\circ}}$	$\frac{k_{47\cdot8^\circ}}{k_{27\cdot8^\circ}}$
Benzene	1·53	1·52	2·33
Chloroform	1·92	1·61	3·09
Nitrobenzene	2·19	1·87	4·08
Acetone	1·93	1·64	3·16
Benzyl alcohol	2·12	2·10	4·44
n-Butyl ,,	2·06	2·10	4·33
Ethyl ,,	2·16	1·98	4·28
Methyl ,,	1·92	1·91	3·68

pendent of temperature, and may therefore be used for the comparison of different reactions over different ranges of temperature.

The mean values of E for this reaction are shown in table IV; R, the gas constant, is taken as 1·985 calories.

TABLE IV.

Solvent.	E.	$k_{37\cdot8^\circ}$.
Benzene	8088	0·000985
Chloroform	10760	0·00186
Nitrobenzene	13470	0·0135
Acetone	11080	0·0269
Benzyl alcohol	14290	0·0440
n-Butyl ,,	14060	0·0550
Ethyl ,,	13910	0·0626
Methyl ,,	12440	0·0748

The value of the temperature-coefficient for this reaction is smaller than is frequently the case; especially is this so in solvent benzene. This suggests the possibility that the reaction is sensitive to light or is photochemical; all the reactions in these papers were conducted in the dark in a covered thermostat.

Experiments in benzene showed that there is no difference in the velocity of this reaction in the dark or in strong sunlight.

The Reaction between Sodium β-Naphthoxide and Ethyl Iodide.

This reaction and the influence of the solvent upon it has been investigated in some detail by the author (T., 1918, **113**, 666, 821; 1920, **117**, 493). It differs essentially from the reaction of bromoacetophenone with aniline, in that it is a dual reaction between ions and molecules of the base (in different proportions in the different solvents) and the molecules of alkyl iodide. It has been shown, too, that there exists some relation between the chemical constitution of the solvent and its effect on the velocity. The details of

the preparation of the solvents and reactants, and the method of measurement, is the same as has been described in the last paper. The temperatures at which the velocity has been measured are 40·0°, 50·5°, and 68·2°. The solvents used are nine alcohols, namely, methyl, ethyl, *n*- and *iso*-propyl, *n*- and *iso*-butyl, *iso*- and *tert.*-amyl and benzyl alcohols; the range of variation of the velocity at any one temperature is about fifteen to one, so that a small but distinct change in the value of the temperature-coefficient is reasonably to be expected. Although there are indications that in some of the associating solvents the reaction is very fast compared with that in the alcohols, it is not possible to measure the velocity under comparable conditions because of the relative insolubility of the sodium salt in them. It has been shown also that the initial concentration has a very large effect on the velocity; this change, due to initial concentration, is not found in the reaction of bromoacetophenone, and a study of the literature suggests that such effect is an indication of the dual nature of the reaction in which it is observed.

A small point here to be noted is that while in the reaction of bromoacetophenone with aniline the precipitation of the salt has no effect on the velocity, in the reaction of sodium naphthoxide the precipitation of the ether formed has a very marked effect in accelerating the reaction; consequently, one is limited to solvents in which the products are completely soluble to nearly normal concentration.

The experimental results are exemplified and summarised in tables V and VI.

TABLE V.

Solvent: iso*Amyl Alcohol.*

Temperature, 68·2°.
N-Ethyl iodide.
N-Sodium naphthoxide.
1·00 c.c. titrated with *N*/25-HCl.

t.	*a* − *x*.	*k*.
0	21·35	—
3	19·75	0·0316
6	18·30	0·0325
9	17·20	0·0314
12	16·00	0·0326
15	15·15	0·0320
	Mean	0·0320

Solvent: n-*Butyl Alcohol.*

Temperature, 68·2°.
N-Ethyl iodide.
N-Sodium naphthoxide.
0·498 c.c. titrated with *N*/25-HCl.

t.	*a* − *x*.	*k*.
0	10·70	—
3	9·20	0·0632
5	8·45	0·0619
7	7·75	0·0632
9	7·15	0·0642
11	6·70	0·0631
	Mean	0·0631

TABLE VI.

Solvent.	$k_{40\cdot0^\circ}$	$k_{50\cdot5^\circ}$	$k_{68\cdot2^\circ}$
Ethyl alcohol	0·00790	0·0212	0·125
*iso*Propyl „	0·00646	0·0177	0·101
Methyl „	0·00460	0·0130	0·0875
n-Propyl „	0·00442	0·0127	0·0868
n-Butyl „	0·00404	0·0107	0·0631
*iso*Butyl „	0·00399	0·0113	0·0525
Benzyl „	0·00273	0·00781	0·0456
*iso*Amyl „	0·00223	0·00649	0·0320
tert.-Amyl „	0·000533	0·00155	0·00987

On plotting the values of $\log k$ *against the reciprocal of the* absolute temperature it is again found that the experimental results are accurately represented by the integrated equation of Arrhenius or of the radiation theory. The mean values of E, the real temperature-coefficient, may, therefore, be calculated with the results set out in table VII, in which the solvents are placed in the order of decreasing velocity.

TABLE VII.

Solvent.	E.	$k_{40\cdot0^\circ}$.
Ethyl alcohol	19840	0·00790
*iso*Propyl „	19990	0·00646
Methyl „	21010	0·00460
n-Propyl „	21300	0·00442
n-Butyl „	19650	0·00404
*iso*Butyl „	19650	0·00399
Benzyl „	20650	0·00273
*iso*Amyl „	20240	0·00223
tert.-Amyl „	21190	0·000533

For the purpose of comparison of the temperature-coefficients of this reaction with those of the addition of bromoacetophenone to aniline, the values of the ratio k_{t+10}/k_t for 37·8° and 47·8° are set out in table VIII, and it will be observed that they are considerably higher in all the solvents than those of the aniline reaction, the velocity of which is much higher at the same temperature in those solvents which are common to the two sets of experiments.

TABLE VIII.

Solvent.	$k_{47\cdot8^\circ}/k_{37\cdot8^\circ}$.	$k_{47\cdot8^\circ}$.
Ethyl alcohol	2·73	0·0188
*iso*Propyl „	2·75	0·0156
Methyl „	2·89	0·0109
n-Propyl „	2·93	0·0105
n-Butyl „	2·70	0·00957
*iso*Butyl „	2·70	0·0100
Benzyl „	2·84	0·00664
*iso*Amyl „	2·78	0·00563
tert.-Amyl „	2·92	0·00128

On the radiation hypothesis some importance attaches to the refractive index of the solvents and its temperature-coefficient strictly the value of n for the infra-red wave-lengths is concerned, but it has been shown that for many liquids the refractive index for the infra-red region is close to that for the visible portions of the spectrum (compare, for example, the results of Seegert, *Diss.*, Berlin, 1908, who finds the refractive index for many liquids in the infra-red, and whose results are not much different from those given for the D-line).* It is therefore sufficient for the present purpose to refer to the temperature-coefficient for the refractive index for the sodium line; the error so introduced will be small. The values of n and its temperature-coefficient for all the solvents are set out in the following table. These have been determined by the author in most cases; reference is given to those taken from the literature (Landolt-Börnstein).

TABLE IX.

Solvent.	n_D at 20°.	dn/dt.
Methyl alcohol [1]	1·3290	0·00040
Ethyl alcohol [2]	1·3617	0·00040
n-Propyl "	1·3849	0·00031
*iso*Propyl "	1·3795	0·00030
n-Butyl "	1·3992	0·00026
*iso*Butyl "	1·3937	0·00046
*iso*Amyl "	1·4053	0·00026
tert.-Amyl "	1·4042	0·00030
Benzyl "	1·5402	0·00037
Acetone	1·3687	0·00039
Benzene [3]	1·5014	0·00065
Nitrobenzene [4]	1·5421	0·00033
Chloroform [5]	1·4462	0·00059

[1] Jahn, *Ann. Phys. Chem.*, 1891, [iii], **43**, 301.
[2] Ketteler, *ibid.*, 1888, [iii], **33**, 508.
[3] Weegmann, *Zeitsch. physikal. Chem.*, 1888, **2**, 237.
[4] Lewis, T., 1916, **109**, 796.
[5] Lorenz, *Ann. Phys. Chem.*, 1880, [iii], **11**, 70.

There is no apparent connexion between the value of n and its temperature-coefficient.

By using Einstein's law of the photochemical equivalent which Lewis shows to be applicable on the radiation theory, the wave-lengths and frequencies of the infra-red radiation absorbed can be calculated. Taking Avogadro's number as $6{\cdot}85 \times 10^{23}$ and Planck's constant as $6{\cdot}55 \times 10^{-27}$, the wave-lengths (in microns) and the frequencies (ν) for the bromoacetophenone reaction are as follows:

* These data are taken from Landolt-Börnstein's tables. Seegert's paper is not accessible in this country.

TABLE X.

Solvent.	Frequency v.	Wave-length (μ).
Benzene	7.57×10^{13}	3·96
Chloroform	9.85×10^{13}	3·04
Nitrobenzene	1.26×10^{14}	2·38
Acetone	1.04×10^{14}	2·89
Benzyl alcohol	1.34×10^{14}	2·24
n-Butyl ,,	1.31×10^{14}	2·29
Ethyl ,,	1.30×10^{14}	2·30
Methyl ,,	1.16×10^{14}	2·58

These are, of course, mean values, as it is not supposed that only one frequency is concerned. For the reaction of sodium naphthoxide with ethyl iodide the values of v and μ are near together and lie between $v = 1.84 \times 10^{14}$, $\mu = 1.63$, and $v = 1.98 \times 10^{14}$, $\mu = 1.51$ respectively.

Discussion of the Results.

It is quite evident that if the application of the radiation theory to the problem of the rôle of the solvent in chemical kinetics is to be accepted, other factors must be considered which may exert a very considerable modifying influence on the true E value, as distinct from that observed, for there is no obvious relation between the observed velocities and their temperature-coefficients. Some of these factors and the question of the legitimacy of comparing reactions in different solvents and of treating the solvent as an added catalyst will now be briefly considered.

The Influence of the Refractive Index of the Solvent.

The equations for the velocity of reaction on the radiation theory are deduced by multiplying the ordinary concentration terms by the radiation density which is supplied by the solvent or added catalyst. This is given by Planck's equation,

$$u_v = \frac{8\pi h v^3 n^3}{c^3} \cdot \frac{1}{e^{-hv/kt} - 1},$$

in which expression h is the universal constant, v is the absorbable frequency, n the refractive index for the wave-length concerned, c the absolute velocity of light, and k the gas constant. The expression shows that the requisite energy supply is proportional to the cube of the refractive index, so that variation of the latter with temperature may be important in modifying the value of E. It has been shown that the value of the temperature-coefficient of the refractive indices of these solvents varies from $dn/dt = 0.00026$

to 0·00065, so that the effect of this on the observed E value may be calculated.

Instead of writing dn/dt, the temperature-coefficient of the refractive index may be expressed by writing $n_t = n_0 - bt$, and when b/n_0 is written β, Lewis (*loc. cit.*) deduces the equation:

$$\frac{d \log k_{ob}}{dt} = \frac{Nh\nu - 3\beta RT^2}{RT^2}.$$

Starting from this equation, the effect of b can be calculated as follows:

$$\frac{d \log k}{dt} = \frac{E}{RT^2} - 3\beta,$$

for by Einstein's law, $E = Nh\nu$. Integrating this expression between the limits T_2 and T_1,

$$\log k_{T_2} - \log k_{T_1} = E/R\left(\frac{1}{T_2} - \frac{1}{T_1}\right) - 3\beta(T_2 - T_1).$$

The effect of this correction is illustrated by calculating the corrected value for E for the first reaction in solvent benzene, for in this liquid β has the greatest value, and so the correction will be greatest. The corrected value for E works out to 8330, using the approximate value for n_0. This correction is not negligibly small when E is compared with the mean uncorrected value 8088 given in table IV; its magnitude is comparable in value with the possible experimental errors, and will not alter the general relationship between velocity and temperature-coefficients.

In the second reaction in the alcohols the correction for the temperature-coefficients of the refractive indices will be smaller than the value calculated out for benzene because β is smaller and the E value to be corrected is larger.

The Effect of Dissociation of the Solute.

This cannot be treated in a precise manner.

The fundamental relationship of the radiation theory is deduced from an equation of the form (for a unimolecular reaction) $dx/dt = A(a-x) \times C_s \times U_v$, where C_s is the concentration of the added catalyst or solvent and U_v is the radiation density, which for simplicity is considered as of a single frequency v. In a bimolecular reaction there will be energy absorbed in quanta by each of the reactants, so that two radiation density terms are concerned. If, however, the reaction is a dual one and the reactants are ionised in solution, both the ions and the molecules are concerned, and there will be energy absorbed in quanta by the ions and the molecules. There will then

be three or four (if both reactants are ionised) characteristic frequencies.

It has been shown in a previous paper that the reaction of sodium naphthoxide concerns ions and molecules of the base, and molecules of the alkyl iodide; three frequencies are therefore concerned.

The work of Acree and others makes it clear that the ions are about five times as reactive as the molecules in these bases. The relation between these factors is expressed by the equation (compare Robertson and Acree, *Amer. Chem. J.*, 1913, **49**, 474),

$$k_{obs.} = \{k_i(a) + k_m(1 - a)\}\ \{1 + f(c)_{salt}\}.$$

So that to correct the values of E obtained for the reactions it is necessary to know the extent of ionisation of the reacting substances in a variety of solvents; also by means of velocity measurements at different concentrations to find the values of k_i and k_m, then to incorporate these into the equations of the radiation theory. Such data are not available at present, but in the author's view this is the explanation of the observed facts in the reaction of sodium naphthoxide, that the temperature-coefficients are not in the inverse order of the velocities. This is borne out by a consideration of the probable extent of ionisation as evidenced by the dielectric constants of the solvents.

Considering the first four alcohols, methyl, ethyl, *n*- and *iso*-propyl, their dielectric constants are similar, and in them it may be supposed that the extent of dissociation is also similar; their other properties also are only slightly varied. In these solvents the temperature-coefficients are inversely as the velocities.

TABLE XI.

Solvent.	Dielectric constant.	$k_{47.8^{\circ}}$.	*E*.
Ethyl alcohol	26	0·0188	19840
*iso*Propyl ,,	26	0·0156	19990
Methyl ,,	32	0·0109	21010
n-Propyl ,,	23	0·0105	21300

n- and *iso*-Butyl alcohols have the same dielectric constants, and in them both the velocity and E are practically the same. With the increasing length of the carbon chain in the higher alcohols the dissociating power, connected with the hydroxyl group, undoubtedly becomes less, so that these members of the series cannot be compared with the lower members from the point of view of probable ionisation.

Also it may be noted that *iso*amyl and benzyl alcohols have simi-

lar dielectric constants (16), and here again the observed temperature-coefficient is inversely as the velocity.

A similar deduction is possible in the reaction of bromoacetophenone (which is not ionised in organic solvents), for whilst there is no apparent relation between the velocity and temperature-coefficient in the whole range of solvents, when similar solvents are compared such relation appears. It is even possible to compare solvents which are not comparable for the other reaction, because in this reaction differences of ionisation do not arise. On comparing the alcoholic solvents used for the bromoacetophenone reaction the relation is quite evident.

TABLE XII.

Solvent.	$k_{47 \cdot 8°}$.	E.
Benzyl alcohol	0·0924	14290
n-Butyl ,,	0·116	14060
Ethyl ,,	0·124	13910
Methyl ,,	0·143	12440

Is the Solvent to be Treated as a Catalyst?

The results of this investigation as a whole indicate clearly that the deductions of the radiation theory are supported by the facts when similar solvents are considered, and when the state of the solute in the solvents is strictly comparable. In dissimilar liquids the relations of temperature-coefficients and velocity are quite discordant. This shows that the influence of a solvent is more than that of a simple catalyst; it actually participates in the reaction. It is on this account that the effect of a solvent is partly constitutive, for if it be supposed that the solvent forms a definite compound or complex with the solute by means of residual affinity (in the sense used by Baly, "Spectroscopy," 1918 edn., 486), it is clear that the velocity will depend upon the constitution of the solvent–solute complex, and this, in turn, will depend on the constitution of the solvent and of the solute. The fact that velocities in different solvents are at all comparable will be due to the dominating influence of the solute on the constitution of the complex. The internal energy of the complex will be specific, so also will be its critical increment; hence, in general, there will be no proportionality in dissimilar solvents between the velocity and the temperature-coefficient. When, however, solvents are chemically similar, and the conditions above referred to respecting the extent of dissociation are fulfilled, then the solvent may be considered purely as a catalyst for the purposes of calculation on the radiation theory,

and the critical increment of internal energy will be less as the velocity increases.

In addition to the experimental data recorded in this paper, the above conclusions are supported by the results of von Halban (*Zeitsch. physikal. Chem.*, 1909, **67**, 129) for different solvents. These results show no relation between the velocity and temperature-coefficients over the whole series of solvents, which are very diverse in kind; but when similar solvents are selected from the list, the values of E are inversely as the velocity (von Halban calculates the A of the Arrhenius equation, which is, of course, proportional to the E of the radiation theory). The figures are shown in table XIII, and refer to the rate of decomposition of triethylsulphine bromide.

TABLE XIII.

Solvent.	k_{70°.	A.
Benzyl alcohol	0·00010	7450
n-Propyl „	0·00018	7380
*iso*Amyl „	0·00045	7260

Summary.

The influence of eight chemically dissimilar solvents upon the temperature-coefficients of the reaction of bromoacetophenone with aniline, and of nine chemically similar solvents upon the reaction of sodium β-naphthoxide with ethyl iodide, has been measured.

The equation of Arrhenius for the effect of temperature does not require any relation between the velocity and temperature-coefficient, but the mathematical development of the radiation theory by Lewis and others requires that the temperature-coefficient of the reaction in the several solvents shall be inversely proportional to the velocity in that solvent.

These experiments have been designed to test this deduction of the radiation theory, and to throw some light on the rôle of the solvent in chemical kinetics by showing to what extent the solvent may be considered as a simple catalyst; and to what extent it has a constitutive effect dependent upon the chemical constitution of the solvent–solute complex.

Temperature-coefficients of the refractive indexes of the solvents for the D-line have been measured, and the effect of this on the temperature-coefficient of the velocity is considered; the effect of dissociation of the solute in the case of the reaction of sodium naphthoxide is also discussed.

It is found that the temperature-coefficient is inversely as the velocity in similar solvents for the reaction of bromoacetophenone,

and for the reaction of sodium naphthoxide in those solvents in which the extent of ionisation is similar; but that the relationship does not hold for dissimilar solvents, so that these cannot be regarded as simple catalysts, and the radiation theory does not apply in such cases.

The radiation theory is therefore supported by these results when allowance is made for the special effects of solvents. The view is taken that reactions proceed by the formation of intermediate solvent-solute complexes, solvent action being a constitutive property by reason of the effect of the solvent on the constitution of the complex.

The author again wishes to record his thanks to Mr. G. Rudd Thompson for providing all facilities for this work.

69, Dock Street,
Newport, Mon. [*Received, November 20th*, 1920.]

XVII.—*Arylazoglyoxalinecarboxylic Acids.*

By Robert George Fargher.

Arylazoglyoxalinecarboxylic acids have been prepared by Burian (*Ber.*, 1904, **37**, 696) by the interaction of sodium diazobenzene-*p*-sulphonate and glyoxaline-4:5-dicarboxylic acid or its 2-methyl or 2-phenyl homologues. Although the reaction involved the loss of carbon dioxide, he assumed the products to be *N*-arylazo-derivatives. Since then (T., 1919, **115**, 217, 1415; 1920, **117**, 668), it has been shown that the arylazoglyoxalines are *C*-azo- and not *N*-azo-derivatives, and that the product of the reaction between sodium glyoxalinedicarboxylate and sodium diazobenzene-*p*-sulphonate is 2-*p*-sulphobenzeneazoglyoxaline-4:5-dicarboxylic acid, and not 1-*p*-sulphobenzeneazoglyoxaline-4-carboxylic acid, as stated by Burian. Nevertheless, combination is accompanied to some extent by loss of carbon dioxide, as quantitative experiments with both glyoxalinedicarboxylic acid and its 2-methyl derivative showed, and, in view of the importance of the 4-arylazoglyoxaline-5-carboxylic acids as intermediate compounds in the synthesis of the purine ring from the glyoxaline nucleus, the reaction has now been submitted to further examination.

p-Bromobenzenediazonium chloride combines readily with 2-phenylglyoxaline-4:5-dicarboxylic acid in sodium carbonate solu-

tion, one of the carboxylic acid groups being displaced by the arylazo-group. The same product, namely, 4-p-*bromobenzeneazo-2-phenylglyoxaline*-5-*carboxylic acid*, is obtained when the mono-carboxylic acid is substituted for the dicarboxylic acid in the reaction.

Similar results are obtained with 2-methylglyoxaline-4:5-dicarboxylic acid, although in this case the reaction appears to proceed rather more slowly.

It had been anticipated that, as the possibilities of benzidine formation had been very largely excluded, the reduction of these compounds with cold stannous chloride solution would lead to the corresponding amino-acids, and that, although subsequent transformation into the glyoxalone might be anticipated in the case of the 2-methyl derivative, unless, indeed, the presence of the adjacent carboxylic grouping proved inhibitive, in that of the 2-phenyl derivative stability might reasonably be anticipated, as it had already been ascertained that the reduction of 4-*p*-bromobenzeneazo-2-phenylglyoxaline led to a substance which almost certainly possessed the constitution 5-amino-4-(2′-amino-5′-bromophenyl)-2-phenylglyoxaline.

This has, however, proved not to be the case. The reaction follows a somewhat novel and unexpected course, the second carboxylic grouping being eliminated during the process of benzidine formation, the acids yielding the same products as the corresponding non-carboxylated glyoxalines.

In view of these results, it appeared to be of interest to examine the reduction of 2-p-*bromobenzeneazoglyoxaline*-4:5-*dicarboxylic acid* under similar conditions. The tendency towards benzidine formation is here sufficiently less pronounced to permit of the isolation as main product of 2-p-*bromobenzenehydrazoglyoxaline*-4:5-*dicarboxylic acid*.

It has already been shown that glyoxalinedicarboxylic acid and its 2-methyl homologue are not acted on by a warm mixture of nitric and sulphuric acids (T., 1919, **115**, 217). 2-Phenylglyoxaline-4:5-dicarboxylic acid reacts under these conditions, but as the composition of the product indicated that substitution had taken place only in the benzene nucleus, its further examination has been omitted.

Experimental.

4-p-*Bromobenzeneazo-2-phenylglyoxaline-5-carboxylic Acid.*

A solution of 6·8 grams of *p*-bromoaniline in 130 c.c. of 10 per cent. hydrochloric acid was diazotised with 2·88 grams of sodium

nitrite and added to an ice-cold solution of 9·23 grams of 2-phenylglyoxaline-4:5-dicarboxylic acid in 400 c.c. of water containing 67·2 grams of sodium carbonate crystals, when gradual separation of a deep orange precipitate took place. After five hours, this was collected. It consisted of the *sodium* salt of 4-p-*bromobenzeneazo-2-phenylglyoxaline-5-carboxylic acid* admixed with that of the unchanged acid. Separation was readily effected by crystallisation from water containing a little sodium carbonate, the former dissolving very sparingly in cold water. The corresponding acid was readily obtained on acidification, and was further purified by crystallisation from alcohol.

4-p-*Bromobenzeneazo-2-phenylglyoxaline-5-carboxylic acid* is insoluble in water and only very sparingly so in alcohol, from which it separates in glistening, red needles, which darken on heating above 160° and effervesce and decompose at 210° (corr.). It dissolves in sulphuric acid, with the production of an eosin-red coloration (Found: C=51·6; H=3·3; N=14·8. $C_{16}H_{11}O_2N_4Br$ requires C=51·6; H=3·0; N=15·1 per cent.).

The *sodium* salt separates from water as a felted mass of orange needles containing $3H_2O$ (Found: loss at 60° in a vacuum=12·0. $C_{16}H_{10}O_2N_4BrNa,3H_2O$ requires H_2O=11·8 per cent. In dried material, Na=5·6. $C_{16}H_{10}O_2N_4BrNa$ requires Na=5·8 per cent.). The same product was obtained when 2-phenylglyoxaline-4-carboxylic acid was substituted for the dicarboxylic acid.

Reduction.—Four grams of the acid were triturated with 25 c.c. of concentrated hydrochloric acid, and gradually treated with 14 c.c. of stannous chloride solution,* the trituration being continued until the completion of the experiment. Evolution of carbon dioxide quickly became evident. The insoluble stannichloride was collected, freed from tin by means of hydrogen sulphide, and the resulting solution evaporated to low bulk under diminished pressure, when separation of a crystalline hydrochloride took place. This was purified by recrystallisation from water containing a little hydrochloric acid, and formed colourless needles melting at 255° (corr.). This was fully identified by analysis (Found: C=45·1; H=4·0; N=13·6. Calc.: C=44·8; H=3·8; N=13·8 per cent.), by the preparation of the triacetyl derivative (Found: N=12·2. Calc.: N=12·3 per cent.), and by its reactions (T., 1919, **115**, 257) as 5-amino-4-(2′-amino-5′-bromophenyl)-2-phenylglyoxaline (T., 1920, **117**, 671).

In an attempt to characterise and compare the two products more completely, it was found that sodium acetate yielded a grey precipitate, which redissolved on adding a little acetic acid and warming,

* Prepared as described in the earlier communications.

and separated in clusters of minute needles melting at 161° (corr.). This proved to be the *monoacetate* of the base (Found: C=52·1; H=4·8; N=14·1. $C_{15}H_{13}N_4Br,C_2H_4O_2$ requires C=52·4; H=4·4; N=14·4 per cent.). Ammonium oxalate yielded a grey precipitate, which darkened rapidly on warming the solution. Addition of excess of sulphuric acid to the concentrated solution of the hydrochloride caused, on stirring, the separation of a sparingly soluble *sulphate*, which crystallised in minute, flattened prisms. Ammoniacal silver nitrate was reduced in the cold.

After separation of the above hydrochloride, no further crystalline material was obtained, as the solution decomposed rapidly on exposure.

The residue, after removal of tin from the soluble stannichlorides, amounted to only 0·5 gram, and consisted mainly of ammonium chloride, although a little *p*-bromoaniline (0·07 gram) was isolated and identified by means of the acetyl derivative.

Reduction with sodium hyposulphite in alkaline solution gave *p*-bromoaniline in a yield amounting to 52 per cent. of the theoretical, but no other pure substance was isolated. The formation of small quantities of a blue dye similar to that obtained by the reduction of nitroglyoxaline was observed.

4-p-*Bromobenzeneazo-2-methylglyoxaline-5-carboxylic Acid.*

This substance was prepared in a similar manner to the 2-phenyl homologue. Starting with 7·52 grams of 2-methylglyoxaline-4:5-dicarboxylic acid, the precipitate which formed was collected (*A*) and the filtrate acidified with hydrochloric acid, when 2 grams of pale orange crystals were obtained. These dissolved somewhat sparingly in alcohol, and separated in glistening, orange needles. The precipitate (*A*) was suspended in water and acidified with hydrochloric acid, when it gave 7 grams of an orange powder, consisting of a mixture of the azo-compound and the unchanged acid. Separation was effected by extraction with, and crystallisation from, alcohol, in which the original acid is practically insoluble, when 5·4 grams of 2-methylglyoxalinedicarboxylic acid were recovered unchanged. In a later experiment, the reaction was allowed to proceed for several hours, but although the yield of the product was larger, it was much darker in colour and more difficult to purify. The ultimate filtrates from the recrystallisation from alcohol yielded a small proportion of a product approximating in composition to 4:5-bis-*p*-bromobenzeneazo-2-methylglyoxaline, but owing to the ease with which resinification took place, it was not obtained pure.

4-p-*Bromobenzeneazo-2-methylglyoxaline-5-carboxylic acid* separates from alcohol, in which it is somewhat sparingly soluble, in orange needles containing $\frac{1}{2}H_2O$. It is very sparingly soluble in water, and dissolves in concentrated sulphuric acid with the production of an orange-red coloration. On heating, it darkens rapidly above 160° (Found: loss at 60° in a vacuum = 3·2. $\frac{1}{2}H_2O$ requires 2·8 per cent. In dried material, C = 43·0; H = 3·2; N = 17·8; Br = 25·4. $C_{11}H_9O_2N_4Br$ requires C = 42·7; H = 2·9; N = 18·1; Br = 25·85 per cent.).

Reduction.—On reduction, as described in the previous case, the evolution of carbon dioxide was again noticed. The insoluble stannichlorides, which accounted for almost the whole of the starting material, yielded 2-methyl-4-(2′-amino-5′-bromophenyl)-5-glyoxalone hydrochloride, which melted at 272° (corr.), the mixture with the reduction product of 4-*p*-bromobenzeneazo-2-methylglyoxaline melting at 272° in the same bath (Found: C = 39·2; H = 3·9; N = 13·7. $C_{10}H_{10}ON_3Br,HCl$ requires C = 39·4; H = 3·85; N = 13·8 per cent.).

The identity was further confirmed by isolation of the base and picrate, and by comparison of the reactions of the bases from the two sources, both of which gave the reactions previously described (T., 1920, **117**, 677).

2-p-*Bromobenzeneazoglyoxaline-4:5-dicarboxylic Acid*.

This was prepared in the manner already described. The precipitate, which formed fairly rapidly, was collected after three hours. The filtrate, on acidification, gave a further quantity of the azo-compound admixed with the unchanged acid. The precipitate was boiled with water containing a little sodium carbonate, leaving a dark brown residue insoluble in sodium carbonate or sodium hydroxide.* The extract, on acidification, gave an orange-red precipitate, which, after boiling with alcohol and drying, darkened above 200° and melted and effervesced at 250° (corr.). It dissolved but sparingly in alcohol, and separated in bunches of minute, red needles, which melted at the same temperature and contained $1C_2H_6O$ (Found, in air-dried material: C = 40·9; H = 3·7; N = 14·6; Br = 21·3; loss at 100° in a vacuum = 11·5. $C_{11}H_7O_4N_4Br,C_2H_6O$ requires C = 40·5; H = 3·4; N = 14·55; Br = 20·75; C_2H_6O = 12·0 per cent. In dried material: C = 39·3; H = 2·4. $C_{11}H_7O_4N_4Br$ requires C = 38·95; H = 2·1 per cent.).

Reduction.—The reduction was carried out as in the previous instances. The decolorised solution from 4 grams of the azo-deriv-

* This is possibly 2:4:5-tris-*p*-bromobenzeneazoglyoxaline.

ative, on dilution with water, gave a precipitate amounting to 3 grams. This dissolved sparingly in water, dilute acids, and the usual organic solvents, but rather more readily in 50 per cent. acetic acid, from which it separated in clusters of minute needles. On heating, these darkened rapidly above 190° and effervesced at 203° (corr.) (Found: loss at 100° in a vacuum = 2·9. $C_{11}H_9O_4N_4Br,\frac{1}{2}H_2O$ requires H_2O = 2·6 per cent. In dried material: C = 39·1, 39·0; H = 3·1, 3·0; N = 16·2, 16·3; Br = 23·8. $C_{11}H_9O_4N_4Br$ requires C = 38·7; H = 2·7; N = 16·4; Br = 23·4 per cent.).

In aqueous solution, the following characteristic reactions were observed: with warm dilute hydrogen peroxide, development of a reddish-brown coloration; with warm ferric chloride, a turbid, orange solution; with warm dilute nitric acid, a bright yellow coloration, whilst silver nitrate and Fehling's solution were reduced on warming.

The composition and properties therefore indicate that the substance is 2-p-*bromobenzenehydrazoglyoxaline*-4:5-*dicarboxylic acid.*

The solution remaining after precipitation of the above substance was freed from tin and evaporated to dryness, leaving 0·7 gram of residue. From this, by suitable means, 0·35 gram of *p*-bromoaniline was isolated and identified, whilst the residual solution then developed a strong odour of ammonia on warming with alkali.

Nitration of 2-Phenylglyoxaline-4:5-dicarboxylic Acid.

A solution of 2 grams of the acid in a mixture of 4 c.c. of nitric acid (D 1·4) and 4 c.c. of sulphuric acid was heated for eight hours on the water-bath, then cooled, poured on ice, and the precipitated product crystallised from 120 parts of boiling water. It separates in small needles, very sparingly soluble in cold water or the usual organic solvents, but readily so in alkalis, with the production of a red coloration. On heating, the substance effervesces at 266° (corr.) (Found: C = 47·9; H = 2·6; N = 15·3. $C_{11}H_7O_6N_3$ requires C = 47·7; H = 2·5; N = 15·2 per cent.).

The composition of the product therefore indicates that nitration has taken place only in the benzene nucleus, and that, as in the case of glyoxalinedicarboxylic acid and its 2-methyl homologue, there is no tendency for displacement of the carboxylic by the nitro-group. In view of the predominating negative character of the glyoxalinedicarboxylic acid substituent, the substance is in all probability 2-m-*nitrophenylglyoxaline*-4:5-*dicarboxylic acid.*

The corresponding *amino-acid* was obtained by reduction with

sodium hyposulphite in alkaline solution. It dissolves readily in dilute mineral acids, but very sparingly in the usual organic solvents, 50 per cent. acetic acid, or hot water, from which it separates in powdery crystals containing $2H_2O$. After treatment with nitrous acid, it develops a deep red coloration on addition to sodium β-naphthoxide (Found: loss at 110° = 12·4. $C_{11}H_9O_4N_3,2H_2O$ requires H_2O = 12·7 per cent. In dried material: N = 16·2. $C_{11}H_9O_4N_3$ requires N = 16·2 per cent.).

WELLCOME CHEMICAL RESEARCH LABORATORIES.

[*Received, January* 14*th*, 1921.]

XVIII.—*The Constitution of Catechin. Part III. Synthesis of Acacatechin.*

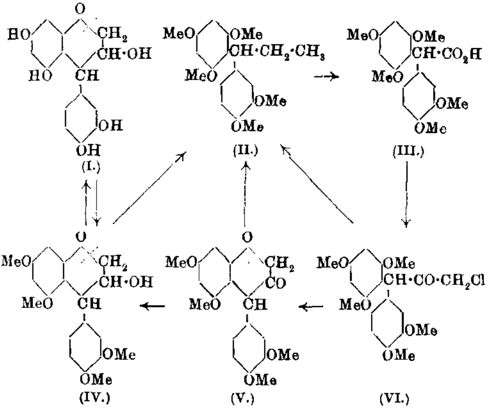
By MAXIMILIAN NIERENSTEIN.

IN the previous communications (T., 1920, **117**, 971, 1151), a provisional formula was suggested for catechin (I). At the same time, it was shown that catechin * tetramethyl ether yields on reduction with metallic sodium and alcohol, and subsequent methylation (compare Kostanecki and Lampe, *Ber.*, 1907, **40**, 720), 3 : 4 : 2′ : 4′ : 6′-pentamethoxy-*aa*-diphenylpropane (II), which substance may be oxidised to 3 : 4 : 2′ : 4′ : 6′-pentamethoxydiphenylacetic acid (III). It was also shown that the acyl chloride of this acid (III) is converted by the action of diazomethane (compare Clibbens and Nierenstein, T., 1915, **107**, 1491) into 3 : 4 : 2′ : 4′ : 6′-pentamethoxydiphenylmethyl chloromethyl ketone (VI), from which 3 : 4 : 2′ : 4′ : 6′-pentamethoxy-*aa*-diphenylpropane (II) is obtained on reduction with metallic sodium and alcohol.

The present communication describes the synthesis of 2 : 4 : 6 : 3′ : 4′-*pentahydroxy-3-phenylchroman* (I). This was carried out according to the following scheme: 3 : 4 : 2′ : 4′ : 6′-pentamethoxydiphenylmethyl chloromethyl ketone (VI) was converted into 4 : 6 : 3′ : 4′-*tetramethoxy-3-phenylchroman-2-one* (V), which was reduced to 2-*hydroxy*-4 : 6 : 3′ : 4′-*tetramethoxy-3-phenylchroman*

* The catechin used was obtained from Merck at Darmstadt in 1911 and 1920. After purification both preparations melted at 175—177°, which is the melting point given by A. G. Perkin and Yoshitake (T., 1902, **81**, 1163, 1173) for catechin from gambier.

(IV). The latter product yielded on demethylation 2 : 4 : 6 : 3′ : 4′-pentahydroxy-3-phenylchroman (I).



On methylation, 2 : 4 : 6 : 3′ : 4′-pentahydroxy-3-phenylchroman (I) yields the original 2-hydroxy-4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman (IV). Both the latter product (IV) and 4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman-2-one (V) give, on reduction with metallic sodium and alcohol, and subsequent methylation, 3 : 4 : 2′ : 4′ : 6′-pentamethoxy-*αα*-diphenylpropane (II), which is in every respect identical with Kostanecki and Lampe's (*loc. cit.*) methylated reduction product from Merck's catechin.

2 : 4 : 6 : 3′ : 4′-Pentahydroxy-3-phenylchroman (I) is in every respect identical with acacatechin, which occurs in *Acacia catechu* (A. G. Perkin and Yoshitake, T., 1902, **81**, 1169; Perkin, T., 1905, **87**, 398). The identity of these two substances is evident from the following comparative summary of melting points and from the fact that there is no depression in the melting points of the respective synthetic products when mixed with acacatechin and its penta-acetyl and pentabenzoyl derivatives, kindly sent by Professor A. G. Perkin.

2 : 4 : 6 : 3′ : 4′-Pentahydroxy-3-phenylchroman sinters at 140°, resolidifies at about 180° on slowly raising the temperature, and melts and decomposes at 204—205°.

Acacatechin sinters at about 140°, resolidifies on slowly raising the temperature, and melts and decomposes at 204—205° (Perkin and Yoshitake, *loc. cit.*, p. 1169).

2 : 4 : 6 : 3′ : 4′-Penta-acetoxy-3-phenylchroman sinters at about 130°, and melts and decomposes at 158—160°.

Penta-acetylacacatechin melts at 158—159° (Perkin, *loc. cit.*, p. 399).

2 : 4 : 6 : 3′ : 4′-Pentabenzoyl-3-phenylchroman melts at 181—183°.

Pentabenzoylacacatechin melts at 181—183° (Perkin and Yoshitake, *loc. cit.*, p. 1171).

2-Hydroxy-4 : 6 : 3′ · 4′-tetramethoxy-3-pheuylchroman melts at 152—153°.

Acacatechin tetramethyl ether melts at 152—154° (Perkin, *loc. cit.*, p. 400).

2-Acetoxy-4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman melts at 136—137°.

Monoacetylacacatechin tetramethyl ether melts at 135—137° (Perkin, *loc. cit.*, p. 400).

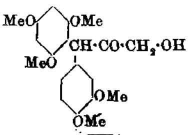
When fused with alkali, 2 : 4 : 6 : 3′ : 4′-pentahydroxy-3-phenylchroman (I) gives phloroglucinol and protocatechuic acid. It has, however, not been possible to identify acetic acid, which is also formed when acacatechin is fused (Perkin and Yoshitake, *loc. cit.*, p. 1170). This is probably due to the small amount of material (2·3 grams) which was used.

Experimental.

4 : 6 : 3′ : 4′-*Tetramethoxy*-3-*phenylchroman*-2-*one* (V).

This substance may be prepared according to either of the ollowing methods:

(*a*) A suspension of 5 grams of 3 : 4 : 2′ : 4′ : 6′-pentamethoxydihenylmethyl chloromethyl ketone (VI) in 50 c.c. of water is igorously heated for thirty-two hours with 20 grams of sodium ydrogen carbonate. The cold solution is filtered and acidified rith dilute hydrochloric acid, when a bulky, white precipitate is ormed. The ω-*hydroxy*-3 : 4 : 2′ : 4′ : 6′-*pentamethoxy*-*αα*-*diphenyl*-



(VII.)

propane-β-one (VII) thus formed crystallises from dilute alcohol in small, prismatic needles, which melt and decompose at 121—122°. It is soluble in the usual organic solvents, with the exception of light petroleum. The yield is 71 per cent. of the theoretical (Found*: C=63·8; H=6·3. $C_{20}H_{24}O_7$ requires C=63·8; H=6·4 per cent.).

ω-Hydroxy-3 : 4 : 2′ : 4′ : 6′-pentamethoxy-αα-diphenylpropane-β-one (VII) is converted into 4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman-2-one (V) by dissolving 5 grams in 50 c.c. of acetic anhydride and heating for eight hours on a water-bath with 25 c.c. of a solution of 4·32 grams (1 mol.) of acetyl chloride in 100 c.c. of acetic anhydride. After reducing the volume to about 50 c.c., water is added, and the precipitate collected and warmed with a dilute solution of sodium hydroxide. The solid remaining is filtered off and freed from alkali. It crystallises from absolute alcohol in small, pointed needles melting at 146—147°. The product is soluble in the usual organic solvents. The yield is 51 per cent. of the theoretical (Found †: C=66·1; H=5·7. $C_{19}H_{20}O_6$ requires C=66·3; H=5·8 per cent.).

(*b*) To a solution of 5 grams of 3 : 4 : 2′ : 4′ : 6′-pentamethoxydiphenylmethyl chloromethyl ketone (VI) in 75 c.c. of dry benzene is added 0·1 to 0·3 gram of aluminium chloride, and the solution heated on a water-bath for twelve to sixteen hours. The solid left on evaporation of the benzene is purified by dissolving in 50 c.c. of 80 per cent. alcohol, filtering, and adding 300 c.c. of water to the filtrate. The precipitate thus obtained crystallises from absolute alcohol in small, pointed needles, which melt at 146—147°. The melting point of a mixture with the substance prepared according to the previous method shows no depression. The average yield of six preparations is 86 per cent. of the theoretical (Found †: C=66·2; H=5·6. Calc.: C=66·3; H=5·8 per cent.).

When condensed with phenylhydrazine in acetic acid solution, the *phenylhydrazone*, $C_{19}H_{20}O_5{:}N_2HPh$, is obtained. It crystallises from acetic acid in yellow needles, which melt and decompose at 236—239° (Found: N=6·5. $C_{25}H_{26}O_5N_2$ requires N=6·4 per cent.).

On reduction with metallic sodium and alcohol, and subsequent methylation with diazomethane, 2 grams of 4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman-2-one (V) gave 1·7 grams of 3 : 4 : 2′ : 4′ : 6′-pentamethoxy-αα-diphenylpropane (II), which melted at 83—84°. This melting point was not depressed when the substance was mixed with (1) the same substance obtained from catechin tetramethyl ether, and (2) the synthetically prepared product (*loc. cit.*, p. 1153).

* Dried at 100°. † Dried at 110°.

2-Hydroxy-4:6:3′:4′-tetramethoxy-3-phenylchroman (IV).

Three grams of 4:6:3′:4′-tetramethoxy-3-phenylchroman (V) dried at 100° are dissolved in 75 c.c. of acetic anhydride and heated in a boiling-water bath for five hours with 20 grams of zinc dust dried at 100°. The filtered solution is diluted with water, and the precipitate collected after twenty-four hours. The crude product is dissolved in 70 c.c. of alcohol and heated for several hours with 20 c.c. of a 20 per cent. solution of sulphuric acid. The product is again precipitated with water and treated in the cold with a 10 per cent. solution of sodium hydroxide, when nearly all the solid dissolves. The filtered alkaline solution is acidified with dilute sulphuric acid, and the precipitate crystallised from alcohol with the aid of animal charcoal. The average yield of five preparations is 62 per cent. of the theoretical. This substance melts at 152—153°, which is the melting point (152—154°) given for acacatechin tetramethyl ether (Found *: C = 65·8; H = 6·6. Calc.: C = 65·9; H = 6·4 per cent.). It differs, however, in one respect from Perkin's acacatechin tetramethyl ether in that it does not give the indigo-blue coloration with acetic and nitric acids observed by him for his product (*loc. cit.*, p. 400). Since this difference might be due to the formation of an isomeric tetramethyl ether during direct methylation of acacatechin, 2 grams of 2:4:6:3′:4′-pentahydroxy-3-phenylchroman (I) were methylated with methyl sulphate according to Perkin's method. The tetramethyl ether obtained in this way melted at 152—153°, and gave Perkin's indigo-blue coloration. Several mixed melting points of these two tetramethyl ethers gave somewhat doubtful depressions of 1·5—2°, but it was found that both yielded on acetylation identical monoacetyl derivatives (m. p. 136—137°), which showed not the slightest depression when their mixed melting point was taken (Found †: C = 64·7; H = 6·4. Calc.: C = 65·0; H = 6·2 per cent.). It is difficult to see why the two tetramethyl ethers should show this difference, unless Perkin's colour reaction is due to a trace of another substance.

Ferric chloride produces a violet coloration if added to a suspension of either 2-hydroxy-4:6:3′:4′-tetramethoxy-3-phenylchroman (IV) or 4:6:3′:4′-tetramethoxy-3-phenylchroman-2-one (V) in concentrated sulphuric acid. This is due to the 3-phenylchroman nucleus (compare Greenwood and Nierenstein, T., 1920, **117**, 1594), and not to the coumaran nucleus, as assumed by Kostanecki and Lampe (*Ber.*, 1906, **39**, 4007). On reduction with

* Dried at 110°. † Dried at 100°.

metallic sodium and alcohol, and subsequent methylation with diazomethane, 3 grams of 2-hydroxy-4:6:3′:4′-tetramethoxy-3-phenylchroman (IV) gave 1·9 grams of 3:4:2′:4′:6′-pentamethoxy-αα-diphenylpropane (II), which melted at 83—84°. This melting point was not depressed by admixture with other preparations of this substance.

2:4:6:3′:4′-*Pentahydroxy-3-phenylchroman* (I).

Four grams of 2-hydroxy-4:6:3′:4′-tetramethoxy-3-phenylchroman (IV) dissolved in 70 c.c. of glacial acetic acid are heated at 130° in a sealed tube for six hours with 4 grams of acetyl chloride.* After opening the tube, the content is at first heated for several hours with 50 c.c. of a 10 per cent. solution of sulphuric acid, hydrogen being passed through continuously. The solution is then concentrated to about 10 c.c. in an atmosphere of hydrogen, diluted with 170 c.c. of water, neutralised with solid barium carbonate, filtered, and extracted several times with ethyl acetate. The residue left on evaporation of the ethyl acetate, dried over anhydrous sodium sulphate, is purified according to Perkin and Yoshitake's method (*loc. cit.*, p. 1163) by crystallising it at first from 25 per cent. alcohol, and subsequently dissolving in boiling ethyl acetate and benzene, from which mixture it separates, with the aid of animal charcoal, in wart-like clusters consisting of small, pointed needles. The average yield of four preparations is 78 per cent. of the theoretical.

2:4:6:3′:4′-Pentahydroxy-3-phenylchroman (I) is in every respect identical with acacatechin (Found †: C=61·9. 62·0; H=4·9, 5·0. Calc.: C=62·1; H=4·8 per cent.). It crystallises, like acacatechin, from distilled water with $3H_2O$ (Found †: H_2O= 15·8. Calc.: H_2O=15·7 per cent.), and gives all the colour reactions of catechin, including the phloroglucinol test with pine-wood and hydrochloric acid (compare Perkin and Yoshitake, *loc. cit.*, p. 1172; Perkin, *loc. cit.*, p. 405).

Both the penta-acetyl derivative (Found ‡: C=60·1; H=5·2. Calc.: C=60·0; H=4·8 per cent.) and the pentabenzoyl derivative (Found ‡: C=73·9; H=4·6. Calc.: C=74·1; H=4·2 per cent.) were prepared according to Perkin's method (*loc. cit.*, p. 399) and

* All attempts to demethylate both 2-hydroxy-4:6:3′:4′-tetramethoxy-3-phenylchroman (IV) and catechin tetramethyl ether (m. p. 144—146°) from Merck's catechin with hydriodic acid have resulted in the production of amorphous substances. Acetyl chloride also gave good results in the case of catechin tetramethyl ether. Thus 5 grams of this substance gave 3·6 grams of catechin, which melted correctly at 175—177°.

† Dried at 160°. ‡ Dried at 100°.

Perkin and Yoshitake's method (*loc. cit.*, p. 1171) respectively. They proved in every respect identical with the corresponding derivatives of acacatechin.

The author's thanks are due to Professor A. G. Perkin for the specimens of acacatechin, penta-acetylacacatechin, and penta-benzoylacacatechin used in this investigation. He also thanks the Colston Society of the University of Bristol for a grant which has covered the expenses of this research.

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XIX.—*Influence of Colloids on the Rate of Reactions Involving Gases. Part I. Decomposition of Hydroxylamine in the Presence of Colloidal Platinum.*

By ALEXANDER FINDLAY and WILLIAM THOMAS.

IT has been shown by Findlay and King (T., 1913, **103**, 1170; 1914, **105**, 1297) that the rate of escape of gas from a supersaturated solution is influenced, in some cases greatly, by the presence of colloids. The influence is a specific one, and is greatly affected by changes in the nature of the colloid.

It was thought that it would be of interest to study the general problem along a different line, and to ascertain the influence of colloids on the velocity of a reaction in which a gas is evolved. By such means, it was hoped, information might be obtained which would throw light on the way in which the colloid acts in retarding or accelerating the evolution of gas from a supersaturated solution. So far as we are aware, no investigation along this line has hitherto been carried out, although Reformatsky (*Zeitsch. physikal. Chem.*, 1891, **7**, 34) studied the velocity of the acid catalysis of methyl acetate in the presence of agar-agar, and found it, as was to be expected, unaffected by the presence of the colloid. It was our intention to study a series of reactions in which gas is evolved both from homogeneous systems (decomposition of diazonium salts, for example) and from heterogeneous systems in the presence of a catalyst, such as colloidal platinum, enzymes, etc. Unfortunately, the carrying out of our plan was interfered with by the war, and

we have been able to make only a preliminary study of one reaction belonging to the second group of reactions mentioned above. As it may be some time before we are in a position to resume and complete the proposed investigations, it is thought advisable to make now a short report on the work so far accomplished.

The reaction first chosen for investigation was the decomposition of hydroxylamine hydrochloride in alkaline solution in the presence of colloidal platinum, a reaction which had been studied to some extent by Tanatar (*Zeitsch. physikal. Chem.*, 1902, **40**, 475). In alkaline solution, hydroxylamine decomposes, for the most part, according to the equation $3NH_2{\cdot}OH = NH_3 + N_2 + 3H_2O$, but about five volumes per cent. of the gas evolved is nitrous oxide, which is formed in accordance with the equation

$$4NH_2{\cdot}OH = 2NH_3 + N_2O + 3H_2O.$$

In the presence of platinum-black as catalyst, the evolved gas consists mainly of nitrous oxide, but a certain amount of nitrogen is also present.

The colloids or semi-colloids, the influence of which on the rate of decomposition of hydroxylamine was studied, were dextrin, starch, gelatin, peptone, and ferric hydroxide (see Findlay and King, *loc. cit.*). The colloidal platinum sol was prepared by Bredig's method, and the sol concentrated by evaporation in a platinum vessel until it had a concentration of 15—16 milligrams per 100 c.c. The same concentration of platinum sol was employed throughout a given series of experiments. The temperature at which the reaction was carried out was 30·6°, and the reaction mixture was agitated by a stirrer driven at a uniform rate and passing through a mercury seal in the stopper of the reaction tube. The gas evolved was collected in a water-jacketed burette filled with a saturated solution of sodium chloride, in which nitrous oxide is soluble only to a negligible extent.

As a result of preliminary experiments, the reaction mixture was chosen as follows: 100 c.c. of platinum sol, 1 gram of hydroxylamine hydrochloride, and 10 c.c. of sodium hydroxide solution containing 60 grams of the solid in 100 c.c. of water. The experimental conditions were alike in all cases. The hydroxylamine hydrochloride and the added colloid, if any, were dissolved in the platinum sol, and the reaction tube containing this solution was placed in the thermostat. The stirrer was then put in motion, and, when a constant rate of stirring was attained, the alkali solution, which had been maintained at the temperature of the bath, was added. After the addition of the alkali, two minutes were allowed to elapse while the necessary connexions were being made, and readings of the volume of gas evolved were then made at

intervals of one minute. To test the apparatus and method of working, a number of experiments were carried out with the above reaction mixture without added colloid. The results obtained were in practically perfect concordance, as is shown in table I. (To economise space, we have given only the volumes of gas evolved at intervals of five minutes in two of the experiments carried out.) In tables II—VI are given, in similar form, the results obtained when to the above reaction mixture the various colloids mentioned above were added. In order that the influence of the addition of colloids may be more readily grasped, some of the experimental results are represented graphically in the accompanying diagram (p. 174).

TABLE I.

Simple Reaction Mixture without Added Colloid.

Time (mins.).	Volume of gas evolved in c.c. I.	II.
1	0·30	0·30
5	2·25	2·25
10	6·50	6·53
15	12·25	12·22
20	19·00	19·00
25	25·25	25·27
30	30·75	30·73
35	35·55	35·55
40	40·33	40·35

TABLE II.

Colloid Added: Dextrin.

Kahlbaum's purest dextrin was employed. An exact weight of the dextrin was dissolved in the platinum sol.

Time (mins.).	Volume of gas evolved in c.c. 1 per cent. solution.	2 per cent. solution.	3 per cent. solution.
1	0·35	0·30	0·30
5	2·30	2·00	1·50
10	5·70	4·20	3·00
15	10·10	6·50	4·75
20	14·75	9·50	6·50
25	19·50	12·50	8·75
30	24·30	15·80	11·50
35	28·50	18·70	13·75
40	31·75	21·00	15·20

TABLE III.

Colloid Added: Starch.

Kahlbaum's pure soluble starch was employed.

Time (mins.).	Volume of gas evolved in c.c. 1 per cent. solution.	2 per cent. solution.	3 per cent. solution.
1	0·30	0·25	0·20
5	2·25	2·00	1·75
10	6·00	5·20	4·25
15	10·80	9·25	7·70
20	16·50	14·00	11·70
25	22·25	19·30	16·20
30	27·75	24·50	21·00
35	32·20	28·80	25·00
40	37·60	32·50	28·00

TABLE IV.

Colloid Added: Gelatin.

French gelatin free from salts was employed.

Time (mins.).	Volume of gas evolved in c.c. 1 per cent. solution.	3 per cent. solution.	5 per cent. solution.
1	0·80	0·50	0·80
5	4·00	3·00	2·50
10	7·30	5·75	5·00
15	10·00	8·20	6·80
20	12·25	10·20	8·20
25	13·80	11·70	8·80
30	15·00	12·30	9·50
35	15·70	12·70	9·75
40	16·25	12·85	9·92

TABLE V.

Colloid Added: Peptone.

Solution A.—The peptone was dissolved in the platinum sol, as in the case of the other colloids.

Solution B.—The peptone was dissolved in the alkali, and the platinum sol added.

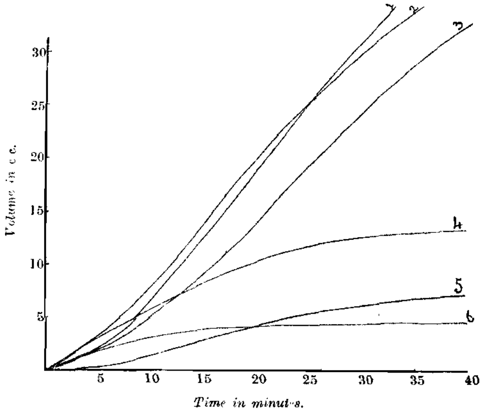
Time (mins.).	Volume of gas evolved in c.c. *A.* 0·25 per cent. solution.	*B.* 0·1 per cent. solution.	0·25 per cent. solution.
1	0·20	0·10	0·10
5	1·50	0·75	0·50
10	3·20	2·20	1·50
15	4·00	3·80	3·00
20	4·25	5·50	4·20
25	4·50	7·00	5·50
30	Platinum coagulated	8·30	6·50
35	and evolution of gas	9·00	7·00
40	practically ceased.	9·50	7·30

TABLE VI.

Colloid Added: Ferric Hydroxide.

The ferric hydroxide sol was prepared by the method of A. A. Noyes (*J. Amer. Chem. Soc.*, 1905, **37**, 94). Concentration, 3·05 per cent.

Time (mins.).	Volume of gas in c.c.	Time (mins.).	Volume of gas in c.c.
1	0·40	25	25·00
5	3·25	30	30·00
10	7·50	35	33·50
15	13·50	40	36·43
20	19·70		



1. No colloid added. 2. 3·05 per cent. ferric hydroxide. 3. 3 per cent starch. 4. 3 per cent. gelatin. 5. 0·25 per cent. peptone (series *B*) 6. 0·25 per cent. peptone (series *A*).

Although it is not possible at the present stage of the work adequately to discuss the effect of colloids on the rate of reactions involving the evolution of gases, there are one or two points to which attention may be directed.

On examining the results obtained, it will be observed that, apart

from the initial stages of the reaction, the effect of added colloids is, in all cases, to retard the rate of reaction as measured by the volume of gas evolved in a given time. This influence of colloids may find an explanation in two different directions. In the first place, one will be inclined to assign the behaviour to an interference by the added colloid with the catalytic activity of the colloidal platinum. An extreme case of this is found in the experiment with peptone, series *A*, where, owing to the inadequate "protection" of the platinum by the peptone, coagulation of the catalyst occurred, and the platinum became practically inactive. From this fact, one might conclude that the varying influence of different colloids in retarding the reaction investigated is due to a difference in the "protective" power of the added colloids on the platinum sol, and to a consequent variation of the extent to which the particles of the platinum catalyst increase in size or aggregate together. Although no actual coagulation of the platinum was observed, except in the case already mentioned, there is, of course, considerable room for variation in the size of particles within the limits of the colloidal state. If we take the protective power of colloids towards platinum sols as being represented, qualitatively at least, by the "gold numbers" of the colloids, we should expect that, of the three colloids, gelatin, dextrin and starch, gelatin (being the most efficient as a protective colloid) should cause a smaller retardation of the reaction than dextrin, and dextrin a smaller retardation than starch. Apart, however, from the initial stages of the reaction, we find the order reversed. The behaviour of peptone, it is true, would agree with the view that the varying influence of colloids is due to variation in their protective power, because the peptone employed, consisting as it did largely of albumoses, has a very feebly protective power, and, indeed, as Zunz (*Arch. int. Physiol.*, 1907, **5**, III, 245) has shown, secondary albumose has slight coagulating power. It must, however, be borne in mind that the protective action of colloids is a specific one in reference to the material protected, and we may be wrong in assuming the order of protective action to be the same for platinum as for gold, but in default of fuller knowledge on this point, we must conclude that variation in the size of the platinum particles is probably not the main cause of the retarding influence of colloids on the reaction under investigation.

A second view which might be taken is that the retarding influence of colloids is due to a contamination of the surface of the platinum particles by adsorption of the added colloid, and to the molecules of the hydroxylamine being thereby prevented from getting access to the platinum catalyst. The literature of "con-

tact catalysis" contains many examples of "poisoning" which may be explained in this way. Thus Bodenstein (*Zeitsch. physikal. Chem.*, 1903, **46**, 730) found that traces of grease diminished the rate at which platinum accelerates the union of hydrogen and oxygen to form water (see also Bancroft, *J. Physical Chem.*, 1917, **21**, 734). As the protective power of a colloid is probably closely related to the extent to which it is adsorbed, the second explanation leads us practically only to the same point as we reached with the help of the former explanation. In either case, however, the behaviour of ferric hydroxide would seem to be anomalous. The electric charge on colloidal ferric hydroxide is opposite in sign to that on colloidal platinum, and complete adsorption of the platinum by the ferric hydroxide no doubt takes place. Yet ferric hydroxide has the least influence of all the colloids studied on the rate of evolution of gas in the reaction under consideration. It may be that ferric hydroxide is itself a weak positive catalyst for the reaction, but this point has so far not been examined.

Whatever may be the importance of the adsorption of colloid by the platinum catalyst as a factor in retarding the catalytic decomposition of hydroxylamine, as measured by the gas evolved, we cannot ignore the fact, already established by Findlay and King (*loc. cit.*), that colloids exercise a very marked and individual action on the velocity with which gases are evolved from solution under conditions where no explanation on the lines of the suggestions already made can be offered. In the present case, therefore, we believe that this specific action of colloids on reactions involving the evolution of gases must also be a factor, the importance of which, however, it is not yet possible to decide. Although a comparison of our results with those obtained by Findlay and King seems to indicate the existence of certain analogies, one has to bear in mind that the processes investigated are not quite comparable. The influence of a colloid on the escape of gas from supersaturated solution is doubtless related in some way to the influence of the colloid on the rate of evolution of a gas from a reaction mixture in which the gas is formed, but the connexion between the two cases is not very clear. We must therefore wait until we are able to investigate the influence of colloids on a reaction which takes place in a homogeneous system and in the absence of a solid catalyst. This investigation will be begun as soon as possible.

CHEMISTRY DEPARTMENT,
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XX.—*Dihydroxynaphthaldehydes.*

By GILBERT T. MORGAN and DUDLEY CLOETE VINING.

THE ten dihydroxynaphthalenes have been submitted to the hydrogen cyanide synthesis for aldehydes, with the result that each of these isomerides has been found to condense with one molecular proportion of the reagent. In this condensation, the dihydroxynaphthalenes display greater reactivity than the three dihydroxybenzenes, only one of which, namely, resorcinol, undergoes the Gattermann condensation.

3:4-*Dihydroxy*-1-*naphthaldehyde* was obtained from 1:2-dihydroxynaphthalene, hydrogen cyanide, and hydrogen chloride in the presence of anhydrous zinc chloride. There was distinct evidence of steric hindrance, which was not overcome by using aluminium chloride as catalyst. In either case, a considerable proportion of unchanged dihydroxynaphthalene was recovered. It is noteworthy that in the case of the other *o*-dihydroxy-derivative, namely, 2:3-dihydroxynaphthalene, there was no sign of this inhibition, the condensation proceeding to completion, with the production of 2:3-*dihydroxy*-1-*naphthaldehyde*.

1:3-Dihydroxynaphthalene (naphtharesorcinol) also condenses readily, yielding 2:4-*dihydroxy*-1-*naphthaldehyde*, whereas in the case of 1:4-dihydroxynaphthalene, steric hindrance is again manifested, a large proportion of the dihydroxy-derivative remaining unchanged, even after prolonged treatment.

Three of the heteronucleal dihydroxynaphthalenes had been condensed in this way by Gattermann (*Annalen*, 1907, **357**, 341), but his observations appear to be of a preliminary character, and we have been able to confirm the results only in one of these three cases. In accordance with the earlier experiments, we find that 2:6-dihydroxy-1-naphthaldehyde from 2:6-dihydroxynaphthalene has properties agreeing with those described for the substance by Gattermann (*loc. cit.*), but, on the contrary, 2:7-*dihydroxy*-1-*naphthaldehyde* from purified 2:7-dihydroxynaphthalene is readily obtained anhydrous, and melts at 159·5—160·5°, whereas the product obtained by Gattermann was stated to contain water ($1H_2O$) and to decompose at 210—215°.

4:8-*Dihydroxy*-1-*naphthaldehyde*, from 1:5-dihydroxynaphthalene, formerly stated to melt at 195—215° (*loc. cit.*), blackens only at 280°, and does not melt below 300° provided that it is obtained free from 4-hydroxy-1-naphthaldehyde. This

impurity arises from the α-naphthol often present in commercial 1:5-dihydroxynaphthalene.

4:5-*Dihydroxy*-1-*naphthaldehyde* is the main product of the hydrogen cyanide condensation with 1:8-dihydroxynaphthalene, but there is indication of a small amount of aldehydic by-product, which may possibly contain an ortho-aldehydic group.

The two heteronucleal αβ-dihydroxynaphthalenes give rise to two pairs of isomeric dihydroxynaphthaldehydes. 1:6-Dihydroxynaphthalene condenses smoothly to 4:7-*dihydroxy*-1-*naphthaldehyde* as main product (yield 60—70 per cent.), and to 2:5-*dihydroxy*-1-*naphthaldehyde* (12—20 per cent.). 1:7-Dihydroxynaphthalene reacts completely, giving 4:6-*dihydroxy*-1-*naphthaldehyde* and 2:8-*dihydroxy*-1-*naphthaldehyde*, the former isomeride being produced in somewhat larger proportion.

The aldehydes having their aldehydic groups in ortho-positions to hydroxyl are easily obtained crystalline, and condense with aniline, yielding yellow to orange dihydroxynaphthylideneanilines (Schiff bases), excepting the Schiff base from 1:4-dihydroxy-2-naphthaldehyde, which is red. The *p*-hydroxyaldehydes of this series are less crystallisable, and give rise to red Schiff bases. Both *o*- and *p*-aldehydes furnish characteristic *p*-bromophenylhydrazones.

EXPERIMENTAL.

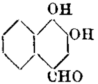
General Methods of Preparation.

(1) *Dihydroxynaphthaldehydes*.—Anhydrous zinc chloride (10 grams), freshly prepared by acting on molten zinc with chlorine, was added to pure dry ether (50 c.c.) in a closed vessel and left until dissolved, the dihydroxynaphthalene (10 grams) and anhydrous hydrocyanic acid (8 c.c.) were then added, and a rapid stream of dry hydrogen chloride was passed into the ethereal solution, contained in a vessel fitted with inlet tube, mechanical stirrer, and reflux condenser. At first the reagents were cooled to 0°, but subsequently the vessel was allowed to acquire the ordinary temperature of the laboratory. The solution gradually assumed a yellow colour, and the intermediate product, an aldimine hydrochloride, separated, usually as a yellow or brown oil. After removing the supernatant ether and washing the product with this solvent, the aldimine hydrochloride was dissolved in cold water (200 c.c.), and the solution warmed, when the sparingly soluble dihydroxynaphthaldehyde separated.

(2) p-*Bromophenylhydrazones of the Dihydroxynaphthaldehydes*, $C_6H_4Br\cdot NH\cdot N{:}CH\cdot C_{10}H_5(OH)_2$.—The dihydroxynaphthaldehyde (0·5 gram), dissolved in the minimum amount of alcohol, was added

lowly, with stirring, to a solution of *p*-bromophenylhydrazine (0·5 gram) in 10 per cent. acetic acid (50 c.c.), when the yellow *p*-bromophenylhydrazone was forthwith precipitated.

(3) *Dihydroxynaphthylideneanilines,* $C_6H_5{\cdot}N{:}CH{\cdot}C_{10}H_5(OH)_2$.—Dihydroxynaphthaldehyde (0·5 gram) and aniline (0·25 gram) were warmed on the water-bath in alcoholic solution for fifteen minutes, when the condensation product separated either immediately from the hot solution or on cooling.

3:4-*Dihydroxy*-1-*naphthaldehyde*, .

The aldimine hydrochloride, separating after three hours as a yellow oil, was dissolved in water, the solution filtered from a dark brown, viscid oil, and the filtrate heated to the boiling point, when it became cloudy and much paler in colour. 3:4-*Dihydroxy*-1-*naphthaldehyde* was precipitated as a yellow, amorphous solid, and was freed from a dark brown, flocculent impurity (m. p. 190—200°) by washing with benzene. A further amount was obtained by boiling the foregoing oil with the aqueous filtrate. It crystallised with difficulty, but was obtained by slow evaporation from ether–petroleum solution in clusters of minute, pale yellow needles, larger crystals having a brown colour. It melted at 178—180° (Found: C=70·09; H=4·54 per cent.). The benzene washings from the crude naphthaldehyde contained unaltered 1:2-dihydroxynaphthalene; the yield of 3:4-dihydroxy-1-naphthaldehyde was only 21 per cent., and this was further diminished during crystallisation by the formation of a dark, resinous product.

The p-*bromophenylhydrazone*, crystallising in yellow needles from alcohol with difficulty, owing to the formation of brown resinous matter, melted at 137—138° (Found: Br=22·72 per cent.).

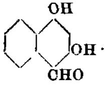
3:4-*Dihydroxynaphthylideneaniline* separated in deep red needles with a green reflex; it melted at 200—202° (Found: N=5·44 per cent.).

Calculated percentages required in the comparison of the foregoing and the following analytical data:

Dihydroxynaphthaldehydes: $C_{11}H_8O_3$ requires C=70·19; H=4·29 per cent.

p-Bromophenylhydrazones: $C_{17}H_{13}O_2N_2Br$ requires Br=22·38 per cent.

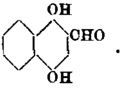
Dihydroxynaphthylideneanilines: $C_{17}H_{13}O_2N$ requires N=5·32 per cent.

2:4-*Dihydroxy*-1-*naphthaldehyde*, 

The condensation reached completion within two hours, the separation of the brown, oily aldimine hydrochloride occurring after twenty minutes. This intermediate product dissolved in 200 parts of water to a brown solution, from the filtrate of which the crude aldehyde separated on warming. Crystallisation from water or dilute alcohol yielded 2:4-*dihydroxy*-1-*naphthaldehyde* in pinkish-brown needles; from alcohol it separated in purplish-brown, acicular prisms, and from benzene–petroleum in almost colourless needles. The various fractions had the same streak on powdering, and melted at 214° (Found: C=69·66; H=4·20 per cent.). It was found difficult to free 2:4-dihydroxy-1-naphthaldehyde from a brown impurity, which was, however, less soluble than the aldehyde in water. This aldehyde is somewhat more soluble than its isomerides in water, alcohol, or benzene; the yield of purified compound was 42 per cent. of the theoretical.

The p-*bromophenylhydrazone*, obtained with difficulty in crystalline form, separated from dilute alcohol in yellow needles melting at 165·5—166·5° (Found: Br=22·06 per cent.).

2 : 4-*Dihydroxy*-1-*naphthylideneaniline* formed lemon-yellow needles, changing to red at 245° and melting at 252° (Found: N=5·58 per cent.).

1:4-*Dihydroxy*-2-*naphthaldehyde*, 

After thirty minutes, the ethereal solution assumed a pale yellow tint, and an almost black, viscid oil slowly separated during two hours. Water (200 c.c.) was added to the oil, when a brown solution was obtained, together with a brown, insoluble residue consisting of impure 1:4-dihydroxynaphthalene. From the filtrate heated to boiling a brownish-yellow, crystalline aldehyde separated, which, when recrystallised from hot dilute alcohol or boiling water, was obtained in silky, greenish-yellow, felted needles melting at 188—190° (darkening at 160—170°) (Found: C=69·42; H=4·55 per cent.).

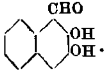
The yield of 1:4-dihydroxy-2-naphthaldehyde, which was only 13·0 per cent. of the calculated amount, was not improved by pro-

longing the reaction for five hours, this alteration leading to an increase in the quantity of coloured impurity.

The p-*bromophenylhydrazone*, a greenish-yellow product crystallising from aqueous alcohol or dilute acetic acid in dark green scales giving a greenish-yellow streak, decomposed without melting at 214° (Found: Br = 22·77 per cent.).

This hydrazone differed markedly from its isomerides, especially in giving rise to intense bluish-red solutions, which became bluer on dilution.

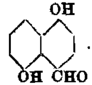
1:4-*Dihydroxy*-2-*naphthylideneaniline* crystallised readily from alcohol in dark red, feathery needles melting at 184—185° (Found: N = 4·88 per cent.).

2:3-*Dihydroxy*-1-*naphthaldehyde*, 

The aldimine hydrochloride separated after fifteen minutes as a yellow oil, which became semi-solid, the reaction being complete in ninety minutes. This product dissolved in water (200 c.c.) to a yellow solution containing only a trace of tarry matter. The aldehyde separated as a bulky, yellow, crystalline precipitate on heating the filtrate to boiling, and crystallised readily from dilute alcohol or from hot benzene in yellow, acicular prisms melting at 133·5—134·5° (Found: C = 70·29; H = 4·42 per cent.). 2:3-*Dihydroxy*-1-*naphthaldehyde* is, with the exception of the 1:8-isomeride, the least soluble member of the series. It is produced with far greater readiness than the aldehydes from the 1:2- and 1:4-dihydroxynaphthalenes, the yield of purified material being upwards of 62 per cent.

The p-*bromophenylhydrazone*, crystallising readily from dilute alcohol in lustrous, yellow scales, melted and decomposed at 200° (Found: Br = 22·87 per cent.).

2:3-*Dihydroxy*-1-*naphthylideneaniline* crystallised readily from alcohol in lustrous, lemon-yellow needles melting at 199—200° (Found: N = 5·57 per cent.).

4:8-*Dihydroxy*-1-*naphthaldehyde*, 

The product obtained by Gattermann (*loc. cit.*) from 1:5-dihydroxynaphthalene was stated to melt indefinitely between 195°

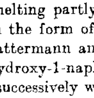
and 215°. We consider that this product was contaminated with 4-hydroxy-1-naphthaldehyde derived from the α-naphthol present in crude 1:5-dihydroxynaphthalene, for in a preparation of aldehyde melting partly between 190° and 200°, the impurity was detected in the form of its Schiff base, 4-hydroxy-1-naphthylidene-aniline (Gattermann and Horlacher, *Ber.*, 1899, **32**, 284).

4:8-Dihydroxy-1-naphthaldehyde, when obtained in a state of purity by successively washing the crude product with warm 50 per cent. alcohol and crystallising the residue from boiling water, separated in minute, yellow needles blackening at 280°, but having no melting point below 300° (Found: C = 69·94; H = 4·20 per cent.). It dissolves readily in ether, but in other solvents it is the least soluble member of the series.

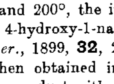
The p-*bromophenylhydrazone*, crystallising readily from dilute alcohol in lustrous, golden-yellow scales, melted and decomposed at 206° (Found: Br = 22·45 per cent.).

4:8-Dihydroxy-1-naphthylideneaniline was obtained in dark red needles melting at 200°, whereas Gattermann gave 194—195° as the melting point (Found: N = 4·98 per cent.).

Aldehydes from 1:8-*Dihydroxynaphthalene*,



Main product (*a*).



By-product (*b*).

The brown, oily, intermediate product collected after two hours was treated with water (200 c.c.), when a yellow solution was obtained, with a considerable amount of black, tarry matter similar to that formed in the alkali fusion of α-naphthol-8-sulphonic acid. The filtrate, after heating to boiling, slowly deposited the greenish-yellow, crude aldehydic material, the main bulk (*a*) of which remained undissolved when extracted in a Soxhlet apparatus with light petroleum; the yellow extract yielded, on evaporation, about 0·8 per cent. of a yellow, crystalline aldehyde (*b*).

4:5-*Dihydroxy*-1-*naphthaldehyde*, the main product (*a*), separated from dilute alcohol in lemon-yellow, nodular crystals darkening at 150—160°, and melting and decomposing at 164—166° (Found: C = 70·70; H = 4·59 per cent.). This isomeride, although insoluble in light petroleum, dissolved more readily in boiling water, benzene, ether, or alcohol; the yield of purified product was about 24 per cent. of the theoretical. Prolonged boiling with water or benzene led to a darkening of the product and to a

ise in melting point, probably owing to a condensation between he *peri*-hydroxyl groups and the aldehydic complex of another nolecule, giving rise, by loss of water, to the compound,

$$C_{10}H_5(OH)_2\cdot CH{<}\substack{C\\O}{>}C_{10}H_5\cdot CHO\,.$$

The presence of a small amount of this condensation product in he specimen analysed would account for the somewhat high result n carbon.

The p-*bromophenylhydrazone*, separating from dilute alcohol in rownish-yellow, felted needles, melted and decomposed at 180° Found: Br = 22·66 per cent.).

4:5-*Dihydroxy*-1-*naphthylideneaniline* was obtained in dark red leedles with slight green reflex, darkening at 200°, but not meltng below 280° (Found: N = 4·68 per cent.).

The by-product (*b*), sparingly soluble in light petroleum, disolved more readily in hot water, alcohol, ether, or benzene, and nelted at 134—135°. The p-*bromophenylhydrazone*, a lemonellow, crystalline powder darkening at 170° and decomposing at 81°, depressed the melting point of the *p*-bromophenylhydrazone f aldehyde (*a*) by 15°. The *dihydroxynaphthylideneaniline* from ldehyde (*b*) formed reddish golden-yellow needles melting at 229—230°. Owing to the small amounts obtained, it was not ossible to subject aldehyde (*b*) and its derivatives to detailed xamination, but the estimation of bromine and nitrogen in the ydrazone and Schiff base, respectively, gave numbers indicating monoaldehyde.

2:6- *and* 2:7-*Dihydroxy*-1-*naphthaldehydes*,

2:6-Dihydroxy-1-naphthaldehyde crystallised from benzene in dark yellow, acicular prisms melting sharply at 189—190° (Gattermann, *loc. cit.*, gives bright yellow needles melting and decomposing at 185—190°); the p-*bromophenylhydrazone* separated from alcohol in minute, yellow scales melting and decomposing at 194—195° (Found: Br = 22·93 per cent.). 2:6-Dihydroxy-1-naphthylideneaniline, orange needles, melted at 250—260° (Gattermann gave orange-red needles with green reflex melting indefinitely at 215—235°) (Found: N = 5·36 per cent.).

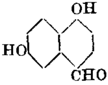
2:7-*Dihydroxy*-1-*naphthaldehyde* was obtained with very little

tarry by-product, the yield being upwards of 70 per cent.; it crystallised from hot water or dilute alcohol in pale yellow, felted needles melting indefinitely at 156·5—158·5°, or from hot benzene in bright yellow, silky needles melting at 159·5—160·5°; crystals from water, after drying between porous tiles for several days, gave C = 67·33; H = 4·87. $C_{11}H_8O_3,\frac{1}{2}H_2O$ requires C = 67·00; H = 4·60 per cent. From benzene: C = 69·72; H = 4·42. $C_{11}H_8O_3$ requires C = 70·19; H = 4·29 per cent.

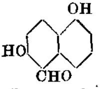
The aldehyde described as 2:7-dihydroxy-1-naphthaldehyde by Gattermann (*loc. cit.*) was stated to melt and decompose at 210—215°, and to crystallise with a molecule of water, which is lost in a vacuum desiccator over sulphuric acid, or more rapidly at 120°. It will be seen below that these properties are approximately those of one of the isomeric aldehydes (*a*) derived from 1:6-dihydroxynaphthalene.

The p-*bromophenylhydrazone* of 2:7-dihydroxy-1-naphthaldehyde crystallised readily from dilute alcohol in shimmering, greenish-yellow scales melting and decomposing at 202—203° (Found: Br = 22·65 per cent.). 2:7-Dihydroxy-1-naphthylideneaniline separated from alcohol in lustrous, yellow needles melting at 214—215° (Found: N = 4·97 per cent.) (Gattermann gave m. p. 195—196°).

Aldehydes from 1:6-*Dihydroxynaphthalene*,



(*a*) Main product.



(*b*) By-product.

The intermediate aldimine hydrochlorides separated rapidly from the reaction mixture, and, after one and a-half hours, the product was washed with ether and decomposed with hot water, when a mixture of isomeric aldehydes was obtained, together with a small quantity of brownish-red impurity and a trace of tarry matter. The isomerides were separated by extraction with chloroform, when the main product (*a*) remained insoluble, whilst the by-product (*b*) passed into solution.

(*a*) 4:7-*Dihydroxy*-1-*naphthaldehyde* (yield, 64 per cent.) crystallised from alcohol in prismatic, silvery needles appearing yellowish-brown by transmitted light and green by reflection; from boiling water it separated in silvery, white needles with a yellowish-brown tint. From both solvents, the aldehyde retained $1H_2O$, darkened at 160°, and decomposed at 218° (Found: C = 63·89;

$H=5{\cdot}03$. $C_{11}H_8O_3,H_2O$ requires $C=64{\cdot}05$; $H=4{\cdot}89$ per cent.). When heated in a vacuum at 120—130°, the foregoing preparations lost water, becoming browner and devoid of silvery lustre. Over sulphuric acid in a vacuum desiccator, this water of hydration was lost very slowly. The anhydrous aldehyde decomposed at 218°, no darkening occurring below 215° (Found: $C=70{\cdot}03$; $H=4{\cdot}51$. $C_{11}H_8O_3$ requires $C=70{\cdot}19$; $H=4{\cdot}29$ per cent.). 4:7-Dihydroxy-1-naphthaldehyde, which dissolved readily in boiling alcohol, was less soluble in hot water, and very sparingly so in benzene or chloroform.

The *p-bromophenylhydrazone* crystallised from dilute alcohol in golden-yellow needles melting and decomposing at 185°; it retained $1H_2O$ (Found: $Br=21{\cdot}34$. $C_{17}H_{13}O_2N_2Br,H_2O$ requires $Br=21{\cdot}30$ per cent. After drying in a vacuum at 120°, $Br=21{\cdot}88$. $C_{17}H_{13}O_2N_2Br$ requires $Br=22{\cdot}38$ per cent.).

4:7-Dihydroxy-1-naphthylideneaniline crystallised from alcohol in orange-red scales with a green reflex; it darkened at 240°, but did not melt below 280° (Found: $N=5{\cdot}11$ per cent.).

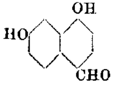
(*b*) *2:5-Dihydroxy-1-naphthaldehyde* (yield about 21 per cent.) was more soluble than its foregoing isomeride, dissolving readily in alcohol or ether, and more sparingly in water, chloroform, or benzene; it crystallised in bright yellow needles, darkening at 190° and decomposing between 225° and 230°. A specimen after drying in a vacuum over sulphuric acid for fourteen days had become anhydrous (Found: $C=69{\cdot}97$; $H=4{\cdot}76$ per cent.).

The *p-bromophenylhydrazone* crystallised from alcohol in yellow needles melting and decomposing at 206—207°; it retained water (Found: $Br=21{\cdot}38$. $C_{17}H_{13}O_2N_2Br,H_2O$ requires $Br=21{\cdot}30$ per cent. After drying as above, $Br=22{\cdot}84$. $C_{17}H_{13}O_2N_2Br$ requires $Br=22{\cdot}38$ per cent.).

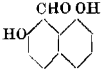
2:5-Dihydroxy-1-naphthylideneaniline crystallised from alcohol in golden-orange needles which melted at 209—210° (Found: $N=5{\cdot}76$ per cent.).

A Possible Third Isomeride.—The filtrate from crystallised 2:5-dihydroxy-1-naphthaldehyde yielded on evaporation a residue, which, after recrystallisation from alcohol, darkened at 170°, melted at 179—184°, and gave with aniline a Schiff base crystallising from alcohol in orange-yellow needles melting at 244—246°; this *anil* (Found: $N=5{\cdot}01$ per cent.) depressed the melting points of the two preceding Schiff bases from 4:7- and 2:5-dihydroxynaphthaldehydes.

Aldehydes from 1:7-Dihydroxynaphthalene.



(*a*) Main product.
(44 per cent.)



(*b*) By-product.
(38 per cent.)

Within twenty minutes, the yellowish-brown aldimine hydrochloride separated, and, after one and a-half hours, the reaction was completed. On treating the crude intermediate product with water, a dark brown, oily solution was obtained containing only a trace of insoluble tar. The filtrate, heated to the boiling point, yielded a greenish-brown product, which was extracted for several days in a Soxhlet apparatus with dry benzene. From this extract the soluble aldehyde (*b*) separated on cooling, whilst the reddish-brown residue consisted of the main product, the less soluble aldehyde (*a*), contaminated with a small amount of dark red impurity, which was left undissolved on extracting the latter aldehyde with hot water.

(*a*) 4:6-*Dihydroxy*-1-*naphthaldehyde* crystallised from boiling water, in which it is sparingly soluble, in yellow, microscopic needles decomposing, without melting, at 265—270° (Found: C=69·42; H=4·11 per cent.). This isomeride, which was readily soluble in ether, dissolved more sparingly in hot alcohol, and was practically insoluble in benzene.

The p-*bromophenylhydrazone*, crystallising from dilute alcohol in greenish-yellow scales with silvery lustre, melted and decomposed at 205—206° (Found: Br=22·47 per cent.).

4:6-*Dihydroxy*-1-*naphthylideneaniline* was formed less readily than in other cases; the reagents were heated under reflux in alcoholic solution for six hours and water was added, when the product separated as a dark red, crystalline powder, decomposing without melting at 230—240° (Found: N=5·44 per cent.).

(*b*) 2:8-*Dihydroxy*-1-*naphthaldehyde* crystallised readily from alcohol in shining, yellow scales melting and decomposing at 203—204°; it was readily soluble in alcohol or ether, and sparingly so in boiling water or benzene (Found: C=69·48; H=4·55 per cent.).

The p-*bromophenylhydrazone* separated from dilute alcohol in minute, bright yellow needles melting and decomposing at 206—207° (Found: Br=21·88 per cent.).

2:8-*Dihydroxy*-1-*naphthylideneaniline* crystallised from alcohol

in lustrous, golden-orange needles darkening at 240°, but not melting below 280° (Found: N = 5·35 per cent.).

We desire to express our grateful thanks to the Salter's Institute of Industrial Chemistry for the grant of a Fellowship to one of us (D.C.V.), which has rendered this collaboration possible.

THE UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [Received, January 20th, 1921.]

XXI.—ortho-*Chlorodinitrotoluenes. Part II.*

By GILBERT T. MORGAN and LESLIE AMIEL JONES.

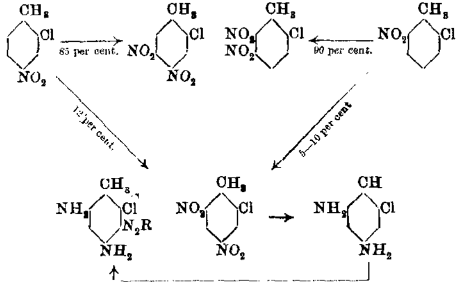
IN the following communication, a new derivation of 2-chloro-4 : 6-dinitrotoluene is indicated, and the reactions of the amino-derivatives of the 4 : 5- and 5 : 6-dinitro-isomerides are further described.

(1) *Nitration of 2-Chloro-6-nitrotoluene.*

Hitherto, the only compound definitely isolated from the nitration of 2-chloro-6-nitrotoluene is 2-chloro-5 : 6-dinitrotoluene (D.R.-P. 107505; Cohn, *Monatsh.*, 1901, **22**, 475, and T., 1920, **117**, 787), but a systematic examination of the product has revealed the existence of 2-chloro-4 : 6-dinitrotoluene (T., 1920, **117**, 786).

2-Chloro-6-nitrotoluene (30 grams), obtained by chlorinating *o*-nitrotoluene, was added gradually to 450 grams of concentrated sulphuric acid and 60 grams of nitric acid (D 1·42) at 20°, the temperature being afterwards raised to 70° for one hour. The product, when poured on ice, yielded a solid and an oil; the former, on crystallising from alcohol, yielded 30 grams of 2-chloro-5 : 6-dinitrotoluene (m. p. 106°) and an oily residue. The oily nitro-compounds were dissolved in warm concentrated sulphuric acid, and the solution, on cooling, deposited more of the 5 : 6-dinitro-compound. The acid filtrate, on dilution with water, yielded an oil, which was dissolved in alcohol, and the concentrated solution seeded with a crystal of 2-chloro-4 : 6-dinitrotoluene, when 1·2 grams of this isomeride separated (m. p. 49°). The filtrate, when diluted with water, yielded an oil, which, on repeating the successive treatments with concentrated sulphuric acid and alcohol, gave a further crop of 2-chloro-4 : 6-dinitrotoluene (II) identical with the

product from 2-chloro-4-nitrotoluene (total yield obtained, 5—10 per cent.); these methods of preparation confirm completely the constitution assigned to the compound.



(I.) (II.) (III.)

(2) *Action of Diazonium Salts on 6-Chloro-2:4-tolylenediamine.*

Benzene-5-azo-6-chloro-2 : 4-tolylenediamine (I).—The preceding dinitro-compound, reduced with alcoholic stannous chloride and hydrogen chloride, yielded 6-chloro-2:4-tolylenediamine (III), the hydrochloride of which, on successive treatment with benzenediazonium chloride (1 mol.) and sodium acetate, gave a brown azo-derivative, crystallising from benzene and petroleum in tufts of stout, red prisms melting at 160° (Found: N = 21·09. $C_{13}H_{13}N_4Cl$ requires N = 21·49 per cent.). A small, dark red residue insoluble in benzene was found to be the *dihydrochloride* of the azo-compound (Found: N = 16·84. $C_{13}H_{13}N_4Cl,2HCl$ requires N = 16·80 per cent.). The *diacetyl* derivative, formed on warming the azo-compound with acetic anhydride, crystallised from alcohol in silky, orange needles melting and decomposing at 267° (Found: N = 16·76. $C_{17}H_{17}O_2N_4Cl$ requires N = 16·26 per cent.).

The *bisazo*-compound, $CH_3{\cdot}C_6Cl(NH_2)_2(N_2{\cdot}C_6H_5)_2$, produced by treating the diamine with excess of benzenediazonium chloride, separated from benzene and petroleum in bright red flakes melting at 192°, and crystallising unchanged from acetic anhydride (Found: N = 23·69. $C_{19}H_{17}N_6Cl$ requires N = 23·05 per cent.).

4′-Nitrobenzene-5-azo-6-chloro-2 : 4-tolylenediamine (I) separated from acetone in dark reddish-black prisms with green reflex; it melted and decomposed at 240—245° (Found: N = 22·53.

$C_{13}H_{12}O_2N_5Cl$ requires N = 22·91 per cent.). The *diacetyl* derivative crystallised from alcohol in red, acicular prisms melting and decomposing at 290° (Found: N = 18·09. $C_{17}H_{16}O_4N_5Cl$ requires N = 17·97 per cent.).

The foregoing azo-compounds give varying shades of orange-red in cold concentrated sulphuric acid.

(3) *Action of Primary Amines on* 4:5- *and* 5:6-*Dinitro-*o-*chlorotoluenes.*

6-*Chloro-4-nitro-*N-*methyl-*m-*toluidine* (V).—Dry methylamine was passed into a solution of the 4:5-dinitro-compound (IV) dissolved in absolute alcohol at 15°. The liquid, which immediately became yellow, afterwards deposited deep red, acicular prisms, the filtrate giving a further crop. The yield was quantitative; the recrystallised product melted at 127° (Found: N = 14·81. $C_8H_9O_2N_2Cl$ requires 13·96 per cent.).

The orientation of the methylamino-group in 6-chloro-4-nitro-*N*-methyl-*m*-toluidine was demonstrated as follows: 6-chloro-4-nitro-*m*-toluidine (VIII) (2 parts) was heated with methyl sulphate (1·5 parts) in toluene solution on the water-bath for about four hours. After distilling off toluene in steam and extracting with ether, the product crystallised from alcohol in long, red, acicular needles (m. p. 126—127°), and was identical with the foregoing preparation.

The *nitrosoamine* (IX), prepared from either specimen, crystallised in yellow plates melting at 70°, and giving Liebermann's reaction (Found: N = 18·35. $C_8H_8O_3N_3Cl$ requires N = 18·30 per cent.).

6-*Chloro-3-nitro-*N-*methyl-*o-*toluidine* (VI), produced by the action of methylamine on 2-chloro-5:6-dinitrotoluene (VII) in alcoholic solution, separated forthwith in orange, acicular prisms softening at 83°, and melting at 84—87°. The velocity of reaction was not so great as in the case of the 4:5-dinitro-isomeride, and the methylamine solution was less coloured; the final yield was, however, almost quantitative (Found: N = 13·90. $C_8H_9O_2N_2Cl$ requires N = 13·96 per cent.).

The orientation of the methylamino-group was demonstrated by heating 6-chloro-3-nitro-*o*-toluidine (XI) with 1 part of methyl sulphate and 2 parts of toluene for two hours at 110°. The product crystallised from alcohol (yield, 70 per cent.) was identical with the preparation obtained by the direct action of methylamine on 2-chloro-5:6-dinitrotoluene.

The *nitrosoamine* (X) from each of these specimens produced

quantitatively in glacial acetic acid solution, crystallised from alcohol in pale yellow, prismatic needles melting at 86—87°, and giving Liebermann's reaction (Found: N = 18·10. $C_8H_8O_3N_3Cl$ requires N = 18·30 per cent.).

6-Chloro-4-nitro-N-phenyl-m-toluidine (V).—2-Chloro-4 : 5-dinitrotoluene was mixed with aniline (2·5 mols.) in warm alcohol, and the solution heated to boiling for thirty-six hours. The colour changed from yellow to intense red, and, on cooling, the liquid slowly deposited reddish-orange crystals, which separated from petroleum in rectangular pyramids melting at 95—96°. Owing to the difficulty of separating the product completely from the reagents, the yield actually obtained was only 50 per cent. of the calculated amount, but no isomeride was detected (Found: N = 10·99. $C_{13}H_{11}O_2N_2Cl$ requires N = 10·67 per cent.).

The orientation of the phenylamino-group was confirmed by an application of the Goldberg condensation (*Ber.*, 1907, **40**, 4541). 6-Chloro-4-nitro-*m*-toluidine (3 grams) was heated under reflux with 15 grams of bromobenzene, 1·5 grams of dry potassium carbonate, and 0·1 gram of cuprous iodide until, on cooling, the deep reddish-brown solution gave crystals of the phenylated base. The liquid was then distilled in steam, the residue extracted with ether, and the product fractionally crystallised from alcohol after boiling with animal charcoal, the yield being upwards of 50 per cent. After crystallisation from glacial acetic acid, the compound separated in reddish-orange prisms melting at 93°, and was identical with the condensation product of aniline and 2-chloro-4 : 5-dinitrotoluene.

The *nitrosoamine*, prepared from either specimen, crystallised from alcohol in yellow prisms melting at 95—96° (Found: N = 14·41. $C_{13}H_{10}O_3N_3Cl$ requires N = 14·40 per cent.).

The filtrate from 6-chloro-4-nitro-*N*-phenyl-*m*-toluidine, obtained by the Goldberg reaction, yielded further quantities of this base and a small amount of a deep red, crystalline compound melting at 128—129° and dissolving in concentrated sulphuric acid to an intense bluish-green solution, the colour of which disappeared on dilution with water.

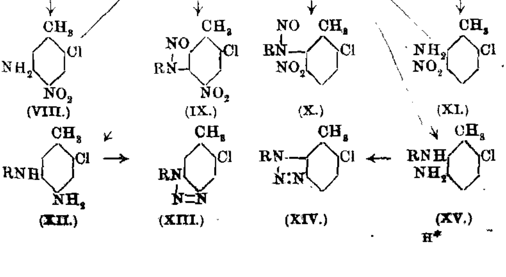
6-Chloro-3-nitro-N-phenyl-o-toluidine (VI) was produced by treating 2-chloro-5 : 6-dinitrotoluene with alcoholic aniline, as in the foregoing preparation. The reaction proceeded very slowly, and, after several weeks, a 50 per cent. yield of orange, rhomboidal plates melting at 108—109° was obtained (Found: N = 10·57. $C_{13}H_{11}O_2N_2Cl$ requires N = 10·67 per cent.).

The constitution of 6-chloro-3-nitro-*N*-phenyl-*o*-toluidine was confirmed by preparing it from 6-chloro-3-nitro-*o*-toluidine by the

Goldberg condensation. 2-Chloro-5-nitro-o-toluidine (4 grams), when heated under reflux for ten hours with bromobenzene (6 grams) in 20 grams of nitrobenzene and in the presence of potassium carbonate (2 grams) and a small amount of cuprous iodide, gave a 75 per cent. yield of 6-chloro-3-nitro-*N*-phenyl-*o-toluidine*. The *solution was distilled in steam to remove nitro*benzene and excess of bromobenzene, and the remaining solid extracted with ether; the residue from the ethereal solution crystallised from light petroleum in orange-red, rhomboidal crystals of the phenylated base, melting at 108—109°, and identical with the preceding preparation. The *nitrosoamine*, prepared from either specimen, crystallised from alcohol in yellow prisms melting at 91° (Found: N = 14·37. $C_{13}H_{10}O_3N_3Cl$ requires 14·40 per cent.).

6-Chloro-3-phenyl-3:4-tolylenediamine (XII), produced by reduction of 6-chloro-4-nitro-*N*-phenyl-*m*-toluidine with zinc dust and ammonium chloride, crystallised from aqueous alcohol in pink needles melting at 109·5°. The *diazoimine* (XIII) was formed on adding sodium nitrite to a glacial acetic acid solution, and precipitated on dilution with water as a creamy-white, flocculent mass; it crystallised from aqueous alcohol in tufts of silky, pink needles melting at 119—120° (*Found*: N = 17·58. $C_{13}H_{10}N_3Cl$ *requires* N = 17·25 *per cent.*).

6-Chloro-2-methyl-2:3-tolylenediamine (XV) was prepared by reducing the 5:6-nitroamine with zinc dust and ammonium



(IV.) (V.) (VI.) (VII.)

(VIII.) (IX.) (X.) (XI.)

(XII.) (XIII.) (XIV.) (XV.)

H*

chloride in aqueous-alcoholic solution, and isolated as the hydrochloride in fine, colourless needles sparingly soluble in water. The free base was obtained as an oil. The *diazoimine* (XIV), produced in glacial acetic acid, crystallised from absolute alcohol in flesh-coloured, prismatic needles melting at 238—239°.

The comparative study of 2-chloro-4:5-dinitrotoluene and 2-chloro-5:6-dinitrotoluene in regard to the displacement of their labile nitro-groups by ammonia and by primary amines (methylamine and aniline) is illustrated by the diagram on p. 191, which also indicates the processes employed in proving the constitution of the products.

Summary.

(1) 2-Chloro-4:6-dinitrotoluene, recently isolated from the nitration product of 2-chloro-4-nitrotoluene, has now been obtained to a similar extent in the nitration of 2-chloro-6-nitrotoluene.

(2) 6-Chloro-2:4-tolylenediamine, the reduction product of the foregoing dinitro-compound, yields azo- and bisazo-compounds of the chrysoidine series comparable with those obtained from its isomeride, 6-chloro-3:5-tolylenediamine (T., 1902, **81**, 97).

(3) The reaction of ammonia and the primary amines (methylamine and aniline) with 2-chloro-4:5-dinitrotoluene leads to the displacement of the 5-nitro-group by the aminic radicle (compare Kenner, T., 1914, **105**, 2717; 1920, **117**, 852). In the case of 2-chloro-5:6-dinitrotoluene, the basic radicle displaces the nitro-group in position 6, and not the 5-nitro-group situated in a sympathetic position with respect to the chlorine and the other nitro-group.

The authors desire to express their thanks to the British Dyestuffs Corporation, Ltd. (Manchester), for facilities afforded in the carrying out of this research.

THE UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

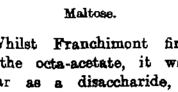
[*Received, December 28th*, 1920.]

XXII.—*The Constitution of the Disaccharides. Part V. Cellobiose (Cellose).*

By Walter Norman Haworth and Edmund Langley Hirst.

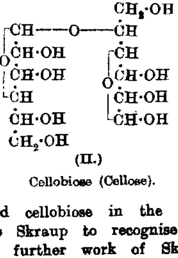
ELLOBIOSE bears much the same relationship to cellulose that naltose does to starch. It is a disaccharide which, like maltose, ives rise on hydrolytic cleavage to two molecular proportions of lucose. Pringsheim submitted cellulose to the action of hermophil and other bacteria, and observed the intermediate ormation of cellobiose in the degradation to glucose (*Zeitsch. hysiol. Chem.*, 1912, **78**, 266). These fermentative processes, nvestigated from the point of view of carbohydrate metabolism in nimals, are related to the fermentative degradation of starch, nd may acquire a new significance in the light of recent ndeavours to utilise cellulose as a source for industrial alcohol.

Although considerable study has been devoted to the constitution of cellulose, the precise mode of linking of the two glucose esidues in cellobiose has hitherto remained obscure. The determination of the structure of this disaccharide may, however, be egarded as an importaut preliminary to the investigation of the arger problem. In an earlier paper by Haworth and Leitch (T., 919, **115**, 809), the constitution of maltose was shown to be epresented by formula I. A constitutional formula (II) was provisionally suggested for cellobiose, and in the present communication this structural representation is supported by experimental proof.



(I.)

Maltose.



(II.)

Cellobiose (Cellose).

Whilst Franchimont first isolated cellobiose in the form of the octa-acetate, it was left to Skraup to recognise the sugar as a disaccharide, and the further work of Skraup and Koenig contributed important data on the preparation and properties of the new biose (*Ber.*, 1901, **34**, 1115; *Monatsh.*,

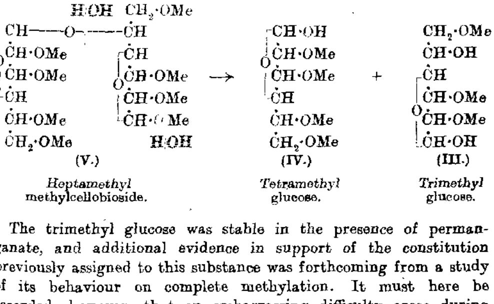
1901, **22**, 1011). An extended study of this new disaccharide by Maquenne and Goodwin (*Bull. Soc. chim.*, 1904, [iii], **31**, 854) and others furnished an alternative procedure for its preparation. In the main, these processes have been followed during the course of the present work. Repeated trials of these methods have revealed, however, extraordinary variations in yield. For no apparent reason, the amount of cellobiose acetate obtained on acetolysis of cellulose was occasionally very small, and therefore it seemed desirable to attempt to improve the recognised procedure. Eventually a process yielding uniformly good results was devised, details of which are to be found in the experimental part of this paper. Relying rather on colour changes than on duration of reaction, the method now described yields results which are dependable.

Cellobiose in the form of its monopotassium derivative was methylated by treatment with methyl sulphate and aqueous sodium hydroxide until most of the hydroxyl groups were protected, and, finally, the introduction of methyl groups was completed by the aid of Purdie's reagents, namely, methyl iodide and silver oxide. Under this exhaustive treatment, the cellobiose yielded an octamethyl derivative in which all the hydroxyl positions were occupied by methoxyl groups. This new derivative was a colourless, crystalline compound, melting at 76—78°, having n_D 1·4643, and showing $[\alpha]_D$ +9° in water, 9·1° in methyl alcohol, and 8·8° in ethyl alcohol. It is herein described as *heptamethyl methylcellobioside*.

The coupling of two hexose residues in a disaccharide molecule proceeds by the linking of one hydroxyl group in each of the component hexoses. Ten hydroxyl groups, then, are available (potentially), two of which are engaged in the above-mentioned union, leaving eight such groups exposed in the disaccharide. In heptamethyl methylcellobioside these eight positions are protected by methyl groups. One of the eight methyl groups may be eliminated by hydrolysis with dilute acids, namely, that protecting the particularly labile reducing group of the biose. Hydrolytic cleavage of the disaccharide linking releases two more hydroxyl groups, namely, those participating in the union of the two hexose residues. The assignment of positions to these newly exposed hydroxyl groups, by investigating the methylated hexoses resulting from the scission of the methylated biose, provides a solution to the problem of the constitution of the disaccharide.

Heptamethyl methylcellobioside was hydrolysed by digestion for three to five hours with 5 per cent. hydrochloric acid at 80°. As cleavage products, two substances were isolated, which were easily separable by extraction with different solvents. Light petroleum

dissolved one component of the mixture, and, from this solution, tetramethyl glucose of the butylene-oxidic type crystallised in the usual characteristic form, and was identified by analysis, by specific refraction and rotatory power, and by mixed melting-point determination with an authentic specimen. The second component of the mixture was soluble in dry ether, and crystallised from this medium in small, colourless needles melting at 115—116°. This compound gave analytical figures corresponding with a trimethyl hexose, and showed $[\alpha]_D$ 68·7° in equilibrium in methyl alcohol. These properties are similar to those of the trimethyl glucose previously isolated by Haworth and Leitch from methylated lactose (T., 1918, **113**, 188), and by Denham and Woodhouse (T., 1914, **105**, 2364) from methylated cellulose, and the constitution is discussed in the former publication. A melting-point determination of this specimen of trimethyl hexose, when mixed with specimens derived from lactose and cellulose, established its identity. The products of cleavage of methylated cellobiose were therefore proved to be butylene-oxidic forms of trimethyl glucose (III) and tetramethyl glucose (IV); consequently, the structure of heptamethyl methylcellobioside is indicated by the formula V.



(V.) Heptamethyl methylcellobioside. (IV.) Tetramethyl glucose. (III.) Trimethyl glucose.

The trimethyl glucose was stable in the presence of permanganate, and additional evidence in support of the constitution previously assigned to this substance was forthcoming from a study of its behaviour on complete methylation. It must here be recorded, however, that an embarrassing difficulty arose during the attempt to introduce two additional methyl groups. One of the hydroxyl groups displayed a tendency to resist methylation to a surprising degree, but by repeated application of the methylating agents, this hindrance was overcome. Finally, 92 per cent. of the original amount of the trimethyl glucose was converted into crystalline tetramethyl-β-methylglucoside, and this was identical in every respect with a specimen previously prepared by Purdie

and Irvine (T., 1904, **85**, 1060). Moreover, this glucoside gave rise on hydrolysis to the butylene-oxidic form of tetramethyl glucose, melting at 84°, and identical in all other respects with an authentic specimen of this compound. Inasmuch as no evidence is available for the assumption that the oxide linking in a sugar is disturbed by the application of the conditions under which the methylation now described was conducted, namely, with the Purdie reagents, the conclusion is drawn that the trimethyl glucose, isolated already from three sources, (*a*) methylated cellobiose, (*b*) methylated cellulose, (*c*) methylated lactose, possesses the butylene-oxidic structure, as shown in the formula (III).

Emulsin and cellase hydrolyse cellobiose, yielding glucose, whilst maltase is without effect. It is not definitely known whether the first of these enzymes owes this property to the presence of traces of the second, which is recognised to be specific in its relation to cellobiose. On other grounds, however, namely, the striking similarity in optical properties of derivatives of lactose and cellobiose (Hudson, *J. Amer. Chem. Soc.*, 1916, **38**, 1566), it is to be regarded as highly probable that the linking of the two hexoses in each is similar, structurally and stereochemically. For these reasons, cellobiose may be considered as glucose-β-glucoside.

Doubtless it is premature to speculate as to the precise form in which the hexoses (or pentoses) must be represented as comprising the cellulose molecule. Recently, various authors have combated the opinion, so generally held, that hexoses as such are grouped together in cellulose as they are in the di- and tri-saccharides. The cumulative evidence, however, points definitely to a structural linking for part of the glucose constituent. This is the glucose fragment linked with other residues through both the reducing group and that hydroxyl group attached to the fifth carbon atom from the reducing end of the hexose chain:

$$\overbrace{\mathrm{CH\cdot CH(OH)\cdot CH(OH)\cdot CH}}^{\mathrm{O}}\mathrm{\cdot CH\cdot CH_2\cdot OH}$$

$$\underset{|}{\overset{|}{\mathrm{O}}}\qquad\qquad\qquad\qquad\underset{|}{\overset{|}{\mathrm{O}}}$$

This mode of linking is probably largely represented in the structure of the cellulose molecule. Inasmuch as trimethyl glucose of the constitution represented by formula III has been isolated, both from methylated cellulose and cellobiose, it seems clear that the above residue forms an essential part of cellulose.

At variance with this view is the opinion expressed by Sarasin (*Arch. Sci. phys. nat.*, 1918, [iv], **46**, 5), who suggests that cellulose is composed of polymerised molecules of *l*-glucosan.

EXPERIMENTAL.

Preparation of Cellobiose Octa-acetate.

The following is a convenient and rapid procedure for the preparation of cellobiose, and, although based on the methods described by Skraup and Koenig and by Maquenne and Goodwin (*loc. cit.*), differs in important respects from the processes outlined by previous workers. Filter paper in layers of four sheets was kept in a dry atmosphere at 20° for three days, and was then cut into pieces of about 1 sq. cm. in size. Twenty grams of this material were stirred into a water-cooled mixture of 80 c.c. of commercial acetic anhydride (85—95 per cent.) containing 11 c.c. of concentrated sulphuric acid. At this stage, the temperature of the viscid mixture was kept just below 20°. When moist filter paper had been used, this treatment produced a marked development of heat, whilst paper too well dried failed to become impregnated with the reagents. Under the prescribed conditions, a viscid paste was formed after stirring the paper with the reagents for five minutes.

A bath, containing calcium chloride and water, having been heated in readiness to a temperature of 120°, the vessel containing the viscid paste of impregnated filter paper was heated by this means, and the contents thoroughly stirred. Rapid disintegration and solution of the paper occurred, the mixture darkened in colour, and, at about 112°, assumed the form of a dark red, mobile liquid, which began to boil. This marked the critical stage of the acetolysis process. Immediately the red solution appeared to be changing to black, the whole of it was poured into 1½ litres of cold water. A pale yellow precipitate of crude cellobiose octa-acetate separated after ten minutes. It was possible to form an immediate judgment on the success of the experiment in the following way: a sample of the precipitate should dissolve in boiling alcohol, but not in the cold; from the hot alcoholic solution, white, powdery crystals should be deposited on cooling; under the cover-glass of a microscope slide, a drop of the hot solution should give characteristic rosettes of needles, affording a rapid and comparatively trustworthy test for the presence of cellobiose octa-acetate.

The pale yellow precipitate was kept in contact with water for six hours, filtered, washed with water, and dried at 40°. It was recrystallised by boiling under reflux for half an hour with 300 c.c. of 90 per cent. ethyl alcohol. While still hot, the solution was filtered, and, on cooling, there separated colourless, minute needles of cellobiose octa-acetate, which, after twelve hours, were collected,

washed with dilute alcohol, and dried. The melting point was 224—227°, but the product may be further purified from alcohol or ethyl acetate. Equally satisfactory results were obtained by using this method of preparation with three times the above quantities. The product weighed 25 to 35 per cent. of the original weight of filter paper, and this yield was maintained throughout an extended series of preparations.

Removal of Acetyl Groups.—In this operation, 10 grams of cellobiose octa-acetate were moistened with a little absolute alcohol and mixed, during constant stirring, with a solution of 12 grams of potassium hydroxide in 50 c.c. of absolute alcohol. After keeping for two hours, the solid potassium cellobiosate which had separated was collected on a filter, washed with alcohol, and dried in a vacuum. The yield was 6 grams, but this product contained traces of free alkali. The free disaccharide was isolated from the potassium derivative by the addition of perchloric acid, as described by Maquenne (*loc. cit.*).

Methylation of Cellobiose: Isolation of Heptamethyl Methylcellobioside.

The cellobiose octa-acetate used in the course of this work melted at 224—227° (uncorr.), showed $[\alpha]_D$ +41·5° in chloroform, and gave by the ebullioscopic method a molecular weight of 685 in chloroform as solvent; the theoretical value is 678.

As the methylation was conducted in alkaline solution, it appeared unnecessary to isolate the free disaccharide from the potassium derivative obtained by removal of the acetyl groups. Accordingly, the potassium cellobiosate (11 grams) was dissolved in a little water and subjected to methylation with 38 c.c. of methyl sulphate and 36 grams of sodium hydroxide dissolved in 70 c.c. of water. The procedure was similar to that followed in the case of lactose (Haworth and Leitch, *loc. cit.*), and the product consisted essentially of a liquid distilling slightly below 200°/0·2 mm. and showing n_D 1·4687, whilst the analytical figures were in agreement for *hexamethyl methylcellobioside* (Found: OMe=48·2. $C_{19}H_{36}O_{11}$ requires OMe=49·3 per cent.).

In all, 72 grams of cellobiose octa-acetate were deacetylated and passed through the methylation treatment, but in order to introduce the full complement of eight methyl groups, the hexamethyl methylcellobioside was digested on three separate occasions with methyl iodide and silver oxide. On fractional distillation of this product, only a minute quantity distilled below 190°/0·25 mm., almost the whole of it being collected at 190—200°/0·02 mm. as a

faintly yellow syrup having n_D 1·4620. This syrup rapidly became completely crystalline, and, after triturating with light petroleum, the colourless crystals melted at 76—78°, showing n_D 1·4643 for the superfused solid (Found: C=52·7; H=8·37; OMe=53·2. $C_{20}H_{38}O_{11}$ [$C_{12}H_{14}O_3(OMe)_8$] requires C=52·86; H=8·37; OMe=54·6 per cent.). The analyses and properties were in agreement with those required for *heptamethyl methylcellobioside*. Polarimetric observations were recorded as follows:

Solvent.	c.	$[\alpha]_D$.
Water	1·560	+9·0°
Methyl alcohol	1·629	9·1
Ethyl alcohol	1·421	8·8
Acetone	1·805	9·9

Hydrolysis of Heptamethyl Methylcellobioside.

A preliminary experiment indicated that complete hydrolysis of the fully methylated cellobiose was effected after heating with 5 per cent. hydrochloric acid for five hours at 80—95°.

Temperature.	Time.	$[\alpha]_D$.
80°	0	+9·0°
80	15 minutes	9·0
80	3 hours	48·2
95	5 „	76·8
95	9 „	76·8

Consequently, 10 grams of heptamethyl methylcellobioside were submitted to a parallel treatment with 500 c.c. of 5 per cent. hydrochloric acid. Thereafter, the mineral acid was neutralised with barium carbonate, filtered, and the solution evaporated to dryness under diminished pressure. The residue of syrup and salts was extracted several times with boiling ether, and yielded 7·7 grams of a clear, yellow syrup. This partly crystallised on nucleation with a specimen of butylene-oxidic tetramethyl glucose.

Separation of the constituents of the syrup revealed the presence of about equal amounts of tetramethyl glucose and of a trimethyl glucose. The former was isolated by repeated digestion with boiling light petroleum, from which, on cooling, the characteristic crystals of the compound were deposited. These melted at 88—89°, showed $[\alpha]_D$ +83·3° in equilibrium in water, and the mixed melting-point determination and other properties were also in full agreement with those recorded for butylene-oxidic tetramethyl glucose (Found: OMe=53·0. Calc.: OMe=52·4 per cent.).

The residual syrup from which the above compound was separated was dissolved in boiling ether. From the cooled solution there were obtained minute, colourless needles melting at

115—116°, which gave analytical figures for a trimethyl glucose (Found: OMe = 41·2. Calc.: OMe = 41·9 per cent.).

The crystalline form, solubility, and melting point were similar to those recorded for the trimethyl glucose isolated by Denham and Woodhouse (*loc. cit.*) from methylated cellulose, and by Haworth and Leitch (*loc. cit.*) from methylated lactose, and mixed melting-point determinations with these specimens indicated their identity. This view was supported by polarimetric observations:

$[\alpha]_D$ (initial value) + 105·0° in methyl alcohol.
(equilibrium value) + 68·7° (after catalysis).

The values given by Haworth and Leitch were respectively + 112·9° (initial) and 69·1° (final).

Conversion of the Crystalline Trimethyl Glucose into Tetramethyl Glucose (Butylene-oxidic). An Example of Steric Hindrance.

When the trimethyl glucose was digested with methyl iodide and silver oxide, it was found that the product remained incompletely methylated. On twice repeating the operation, the boiling point (120°/0·9 mm.) and refractive index (n_D 1·4512) of the product showed higher values than were anticipated (b. p. 116°/0·9 mm. and n_D 1·4454), indicating that methylation of the whole of the material was incomplete. Only after five methylations was the major portion (92 per cent.) of the product obtained as a liquid distilling at 115—117°/0·9 mm. and showing n_D 1·4457, which values correspond with those recorded for tetramethyl β-methylglucoside (Haworth, T., 1915, **107**, 12). The distillate partly crystallised on nucleation with an authentic specimen of this substance, and, after draining on porous tile, the crystals melted at 38—39°, as previously observed by Purdie and Irvine (*loc. cit.*), and a mixed melting-point determination showed no depression (Found: OMe = 61·3. Calc.: OMe = 62·0 per cent.). The remaining 8 per cent. of the quantity of distilled product showed n_D 1·4492, and contained only 57·3 per cent. of methoxyl.

Hydrolysis of the crystalline tetramethyl β-methylglucoside proceeded normally on digestion with 8 per cent. hydrochloric acid for three hours. On isolating the free sugar in the usual way, it crystallised readily and completely, melted at 80—84°, and showed n_D 1·4585 for the superfused solid, which is comparable with the value 1·4588 previously observed (Haworth, *loc. cit.*). Moreover, a mixture with an authentic specimen of butylene-oxidic tetramethyl glucose melted at 80—83°. The specific rotatory power in equilibrium in water was + 83°. All the above

properties are in good agreement with those previously quoted in the literature for this compound.

The authors are grateful to the Carnegie Trust for a Scholarship, under the terms of which this investigation has been conducted.

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[*Received, January 3rd, 1921.*]

XXIII.—*Derivatives of Gallic Acid. Part II. Gallic Acid (and the Cresotic Acids) and Chloral.*

By RUPCHAND LILARAM ALIMCHANDANI and ANDREW NORMAN MELDRUM.

THE condensation of chloral with methoxybenzoic acids was studied first by Fritsch (*Annalen*, 1897, **296**, 358; 1898, **301**, 360), and the study has been continued by Meldrum (T., 1911, **99**, 1712), by Bargellini and Molina (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 146), and by the authors (T., 1920, **117**, 964). Little, if anything, has been done on the condensation of chloral with the hydroxybenzoic acids. The authors undertook to investigate the condensation with gallic acid; then, in order to throw light on the results they obtained, they found it desirable to extend the work to the cases of *p*-, *o*-, and *m*-cresotic acids.*

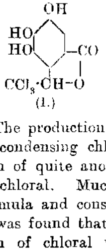
The condensation with gallic acid was undertaken as a possible means of ultimately obtaining 3:4:5-trihydroxyphthalic acid (II). The trimethyl ether of this acid has been synthesised by Bargellini and Molina (*loc. cit.*) and by the authors (*loc. cit.*),† but has not

* The work with *m*-cresotic acid has led to the isolation of three substances, and these are still under investigation. The results will be communicated later, when the constitution of the substances has been established.

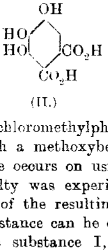
† The same acid has been synthesised recently by Herzig and Brunner (*Annalen*, 1920, **421**, 283). In each case the same synthetic method was employed and the initial material was the trimethyl ether of gallic acid (or its ester). Herzig and Brunner found it necessary to resort to methylation in the course of the work. Alimchandani and Meldrum had the same experience previously. The explanation is that, in the condensation with chloral, the sulphuric acid that is employed as condensing agent can hydrolyse the trimethyl ether of gallic acid to the dimethyl ether, namely, syringic acid, which then condenses with chloral. Herzig and Brunner do not state that this explanation had already been given, and do not give any explanation themselves of the necessity for methylation. Bargellini and Molina found that the condensation proceeded without disturbance.

been completely hydrolysed. The constitution II used to be ascribed to pyrogalloldicarboxylic acid, but this acid is believed now to have the constitution III (Voswinckel and de Weerth, *Ber.*, 1912, **45**, 1242; Feist, *Arch. Pharm.*, 1907, **245**, 586; 1918, **256**, 1). It was hoped to synthesise 3:4:5-trihydroxyphthalic acid and to compare it with pyrogalloldicarboxylic acid directly. Although this hope was not fulfilled, in the course of the work that was carried through, compounds were obtained that merit description.

From chloral and gallic acid, with sulphuric acid as the condensing agent, three different substances can be obtained. When excess of gallic acid is used, the product is 3:4:5-*trihydroxy-2-trichloromethylphthalide* (I). This substance would seem capable of conversion, by hydrolysis, into a phthalidecarboxylic acid, and this, ultimately, into 3:4:5-trihydroxyphthalic acid (II). Hydrolysis, however, did not lead to any definite product; the trichloromethylphthalide contains the three hydroxy-groups of the gallic acid, and behaves much like this acid on treatment with alkali, giving material of indefinite composition.



(I.)



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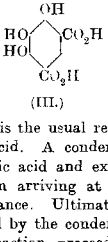


(III.)

The production of a trichloromethylphthalide is the usual result of condensing chloral with a methoxybenzoic acid. A condensation of quite another type occurs on using gallic acid and excess of chloral. Much difficulty was experienced in arriving at the formula and constitution of the resulting substance. Ultimately, it was found that the substance can be obtained by the condensation of chloral with the substance I, the reaction proceeding according to the equation

$$C_9H_5O_5Cl_3 + 2CCl_3{\cdot}CHO = C_{13}H_5O_6Cl_9 + H_2O.$$

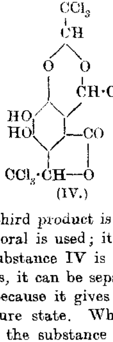
Once this formula had been arrived at, it was easy to devise constitution IV for the substance, on the basis of the following behaviour:

(1) When treated with a cold alkaline solution, the substance does not decompose, whilst I, under the same treatment, darkens as readily as gallic acid.

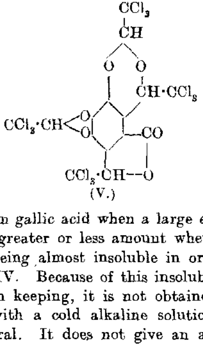
(2) It gives rise to disodium, dipotassium, dimethoxy-, diacetyl, and dibenzoyl derivatives.

(3) With ferric chloride solution, it gives a deep green coloration, such as is given by catechol.

These properties might well be expected of a substance containing the two hydroxyl groups shown in IV. What could not have been expected is the great stability which the substance shows under treatment with alkali. It is true that when boiled with an alkaline solution the substance decomposes, without yielding definite products; in this case, decomposition must begin at the two hydroxyl groups. On the other hand, the dimethoxy- and dibenzoyl derivatives of the substance can be prepared from it in the usual manner, that is, in the presence of alkali. Moreover, these derivatives, and the diacetyl derivative as well, do not decompose when heated with sodium hydroxide solution. Evidently the phthalide ring with its $>CH{\cdot}CCl_3$ group, and the new ring, containing two oxygen atoms and two $>CH{\cdot}CCl_3$ groups, are each remarkably stable.



(IV.)



(V.)

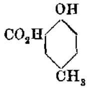
A third product is obtained from gallic acid when a large excess of chloral is used; it is found in greater or less amount whenever the substance IV is prepared. Being almost insoluble in organic liquids, it can be separated from IV. Because of this insolubility, and because it gives off chloral on keeping, it is not obtained in the pure state. When treated with a cold alkaline solution, it yields the substance IV and chloral. It does not give an acetyl derivative. Its whole behaviour is in accordance with the constitution V.

p-Cresotic acid (VI) reacts with chloral according to the equation

$$C_8H_8O_3 + 2CCl_3{\cdot}CHO = C_{12}H_8O_4Cl_6 + H_2O.$$

Constitution VII has been assigned to the substance in view of the facts that with ferric chloride it does not give the violet coloration characteristic of salicylic acids, and that it is acid to litmus and forms salts easily.

Thus the same heterocyclic ring, containing two oxygen atoms and two $>CH{\cdot}CCl_3$ groups, is present in the substances IV and VII. Like IV, VII is remarkably stable under treatment with a hot alkaline solution. When boiled with zinc dust and acetic acid, VII gives rise to the substance VIII, which is a derivative of phenylethylidene chloride. In this connexion, it is to be recalled that Pinner (*Ber.*, 1898, **31**, 1935), using the same reagents, converted the two $\cdot CCl_3$ groups in hexachlorodimethyltrioxine (XV) into $\cdot CHCl_2$ groups, the trioxine ring itself undergoing no change. In the present case, the heterocyclic ring breaks down, and the resulting $\cdot CH(OH){\cdot}CCl_3$ group is converted into $\cdot CH_2{\cdot}CHCl_2$. Compound VIII, when fused with potassium hydroxide, gives rise to IX. Both these compounds, VIII and IX, give with ferric chloride the violet coloration characteristic of salicylic acids.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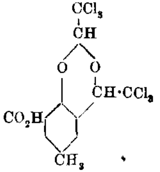
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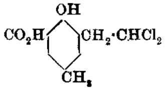
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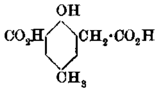
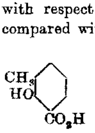
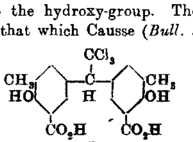

(IX.)

The reaction of chloral with *o*-cresotic acid (X) proceeds according to the equation

$$2C_8H_8O_3 + CCl_3{\cdot}CHO = C_{18}H_{15}O_6Cl_3 + H_2O.$$

The product has the constitution XI, the assumption being made that chloral attacks the cresotic acid molecule at the para-position with respect to the hydroxy-group. The substance XI is to be compared with that which Causse (*Bull. Soc. chim.*, 1890, [iii], **3**,


(X.)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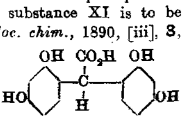

(XII.)

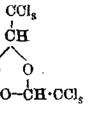
861) obtained from chloral and resorcinol, and which Hewitt (T., 1896, **69**, 1265) showed to have the constitution XII.

Thus the condensation of a hydroxybenzoic acid with chloral can take place in at least three different ways:

(*A*) As in the case of a methoxybenzoic acid, a trichloromethylphthalide is formed; gallic acid, when used in excess, gives the trichloromethylphthalide (I).

(*B*) A new heterocyclic ring is formed; *p*-cresotic acid gives rise to the substance VII. Gallic acid also, when taken with excess of chloral, gives the compound IV, containing the new heterocyclic ring along with the phthalide ring. The new ring is remarkable for stability under treatment with alkaline solution. Under this treatment, the substance VII is not hydrolysed. The substance IV is, of course, vulnerable to attack by alkali, by reason of its two hydroxy-groups, but the dimethoxy-, diacetyl, and dibenzoyl derivatives of IV are as stable as the substance VII. Here the stability also of the phthalide ring and of the $\cdot CCl_3$ group attached to it is worthy of note.

Chloral has a strong tendency to take part in the formation of heterocyclic rings. Wallach obtained substances, which he termed chloralides, by the condensation of chloral with glycollic, malic, tartaric, and trichlorolactic acids. The first known chloralide (XIII) he obtained from chloral and trichlorolactic acid (*Annalen*, 1878, **193**, 1). From salicylic acid he obtained the substance XIV. The heterocyclic rings in XIII and XIV, however, are different from one another and from the heterocyclic ring which



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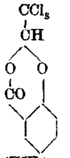

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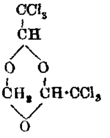

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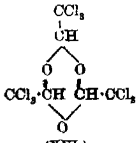
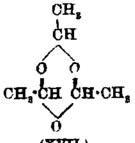


(XVI.)



(XVII.)

is present both in IV and VII. The nearest approach to this new ring is to be found in hexachlorodimethyltrioxine (XV), which Pinner obtained by the action of chloral on formaldehyde in the presence of sulphuric acid (*loc. cit.*). Various meta-chlorals have been described, one of which may have the constitution XVI. Both XV and XVI have the same ring structure as paraldehyde (XVII).

(*C*) In the case of *o*-cresotic acid, two molecules of the acid condense with one molecule of chloral, and the substance XI is formed. No closed chain is produced; formation of the new heterocyclic ring is impossible, owing to the position of the hydroxy-group, and formation of the phthalide, which appears possible, does not take place.

EXPERIMENTAL.

3:4:5-*Trihydroxy-2-trichloromethylphthalide* (I).

Gallic acid (24 grams), chloral hydrate (10 grams), and sulphuric acid (100 c.c. of 94—95 per cent.) were mixed together, and the solids dissolved by vigorous shaking. After about forty-eight hours, the liquid was cooled by a freezing mixture, when some gallic acid separated. The mixture was filtered, the filtrate poured on ice, and the white solid which separated was collected, washed, and crystallised from hot water; the yield was 10 grams. On recrystallisation from a mixture of acetone and chloroform, it separated in double pyramids melting at 210—212° (Found: Cl = 35·55. $C_9H_5O_5Cl_3$ requires Cl = 35·54 per cent.).

The *triacetyl* derivative was prepared by the aid of acetic anhydride in the presence of a few drops of concentrated sulphuric acid. It crystallised from absolute alcohol in white, lustrous, silky needles melting at 172° (Found: Cl = 25·12. $C_{15}H_{11}O_8Cl_3$ requires Cl = 25·02 per cent.).

Hydrolysis of these substances did not lead to definite results. When treated with an alkaline solution, the former darkened at once, and no new substance could be isolated from the solution. When it was heated with water in sealed tubes, part was unchanged and part was converted into tarry products. No better result was obtained by heating the substance with water and lead oxide or with water and potassium hydrogen sulphate.

Lactone of 7:8-Dihydroxy-2:4-bistrichloromethyl-6-β-trichloro-α-hydroxyethyl-1:3-benzdioxine-5-carboxylic Acid (IV, p. 203).

Gallic acid (24 grams), chloral hydrate (40 grams), and sulphuric acid (200 c.c. of 94—95 per cent.) were mixed together, when the

solids dissolved. After about twenty-four hours, a gelatinous mass separated, floating on the surface of the liquid, the amount of which increased in course of time. On the fourth day, the solution, together with the floating mass, was poured on ice, when a white solid separated, which was collected, washed with water, and dried on porous tile; the yield of the crude product was 40 grams. It crystallised from either methyl alcohol or ethyl alcohol in transparent, stout plates containing alcohol of crystallisation. It effloresced at the ordinary temperature, lost alcohol completely at 100—110°, and then melted and decomposed at 277—279° (the melting point being determined quickly) (Found: MeOH = 10·00. $C_{13}H_5O_6Cl_9$,2MeOH requires MeOH = 10·00 per cent. EtOH = 13·62. $C_{13}H_5O_6Cl_9$,2EtOH requires EtOH = 13·76 per cent. Cl = 55·56. $C_{13}H_5O_6Cl_9$ requires Cl = 55·43 per cent.).

Disodium Compound.—The substance was dissolved in very dilute, cold sodium hydroxide solution, and to this a concentrated solution of the alkali was added. A yellow *sodium* compound separated, which was collected, washed with a small amount of water, and then crushed on a porous tile (Found: Na = 7·47. $C_{13}H_3O_4Cl_9(ONa)_2$ requires Na = 7·42 per cent.).

Dipotassium Compound.—A yellow *potassium* compound was obtained in the same manner as the sodium compound (Fouud: K = 11·76. $C_{13}H_3O_4Cl_9(OK)_2$ requires K = 11·96 per cent.).

Dimethoxy-derivative.—The substance (5 grams) was dissolved in methyl sulphate (20 c.c.) with heating. To this, a solution of potassinm hydroxide was added, when a vigorous reaction took place, which was checked by cooling. Addition of the alkali was continued until the solution was faintly alkaline. A brown, sandy material separated, which was collected and dried. It crystallised from glacial acetic acid in colourless, prismatic needles, and, after recrystallisation from acetone, melted at 192—193° (Found: Cl = 52·80. $C_{15}H_9O_6Cl_9$ requires Cl = 52·85 per cent.).

The *diacetyl* derivative was prepared by means of acetic anhydride in the presence of a few drops of concentrated sulphuric acid. It crystallised from glacial acetic acid in clusters of prismatic needles, and, when recrystallised from absolute alcohol, melted at 217—219° (Found: Cl = 48·31. $C_{17}H_9O_8Cl_9$ requires Cl = 48·37 per cent.).

Dibenzoyl Derivative.—The substance (2 grams) was dissolved in benzoyl chloride (10 c.c.) with heating. To this, a slight excess of sodium hydroxide solution was added, when a vigorous reaction took place and an oil separated, which solidified when treated with water. When crystallised from glacial acetic acid and then from absolute alcohol, it formed slender, prismatic needles melting at

234—236° (Found: Cl = 40·5. $C_{27}H_{18}O_8Cl_9$ requires Cl = 40·7 per cent.).

Lactone of 7 : 8-βββ-Trichloroethylidenedioxy-2 : 4-bistrichloromethyl-6-βββ-trichloro-α-hydroxyethyl-1 : 3-benzdioxine-5-carboxylic Acid (V, p. 203).

Gallic acid (20 grams), chloral hydrate (60 grams), and sulphuric acid (250 c.c. of 94—96 per cent.) were mixed together, and, on vigorous shaking, most of the solid dissolved. The impurities were filtered off. During the course of three days, a solid separated, which was collected, and dried on porous tile. The dried material contained a quantity of the substance IV, which was removed by extracting the material thrice with acetone. The yield of the insoluble product was 10 grams.

It is an amorphous powder insoluble in most organic liquids. It begins to char at about 250°, and, when quickly heated, melts at 268—270° (Found: Cl = 64·3. $C_{15}H_4O_6Cl_{12}$ requires Cl = 60·3 per cent.).

6-Methyl-2 : 4-bistrichloromethyl-1 : 3-benzdioxine-8-carboxylic Acid (VII, p. 204).

p-Cresotic acid (20 grams), chloral hydrate (40 grams), and sulphuric acid (150 c.c. of 98—100 per cent.) were mixed together. On vigorous shaking and slight warming, the solids dissolved. After five days, the solution was poured on ice, when a yellowish-white solid separated, which was collected, washed with water, and dried. The product was a mixture of the condensation product and unaltered *p*-cresotic acid. The latter was removed by grinding the material with a small quantity of absolute alcohol, in which the cresotic acid was extremely soluble, and the derivative sparingly so; the yield was 20 grams. The substance was sparingly soluble in most organic solvents; from acetone it crystallised in fine, snow-white needles melting and decomposing at 285—286° (Found: Cl = 49·7. $C_{12}H_8O_4Cl_6$ requires Cl = 49·9 per cent.).

Sodium Salt.—The substance was dissolved in dilute sodium hydroxide solution, and to this a concentrated solution of the alkali was added, when a white, crystalline *sodium* salt was obtained (Found: Na = 5·29. $C_{12}H_7O_4Cl_6Na$ requires Na = 5·11 per cent.).

4-Hydroxy-5-ββ-dichloroethyl-m-toluic Acid (VIII, p. 204).

The substance (VII) (2 grams) and glacial acetic acid (40 c.c.) were boiled together, but the solid did not dissolve completely.

To the hot mixture, zinc dust (10 grams) was added in small amounts, when a vigorous reaction took place, and the undissolved material dissolved freely. Heating was continued for about an hour, after which time water (60 c.c.) was added, and the mixture boiled for fifteen minutes more. The hot solution, having been filtered, gave, on cooling, white, needle-shaped crystals, which, when recrystallised from benzene, melted at 205—207° (Found: Cl = 28·8. $C_{10}H_{10}O_3Cl_2$ requires Cl = 28·5 per cent.).

The *calcium* salt is characteristic. It crystallises in slender, glistening needles (Found: H_2O = 11·7. $C_{20}H_{18}O_6Cl_4Ca,4H_2O$ requires H_2O = 11·9 per cent.). The anhydrous salt was also analysed (Found: Ca = 7·53. $C_{20}H_{18}O_6Cl_4Ca$ requires Ca = 7·48 per cent.).

6-*Hydroxy*-5-*carboxy*-m-*tolylacetic Acid* (IX, p. 204).

The substance just described (2 grams) and potassium hydroxide (10 grams) were fused together in a nickel crucible at 250—260° for about half an hour. The product was dissolved in water and acidified, when brown-coloured needles were obtained. From acetic acid, it crystallised in white, soft needles melting and decomposing at 257° (Found: C = 57·3; H = 4·9. $C_{10}H_{10}O_5$ requires C = 57·1; H = 4·8 per cent.).

The *silver* salt was prepared (Found: Ag = 50·8. $C_{10}H_8O_5Ag_2$ requires Ag = 50·9 per cent.).

ββ β-*Trichloro*-4 : 4′-*dihydroxy*-αα-*di*-m-*tolylethane*-5 : 5′-*dicarboxylic Acid* (XI, p. 204).

o-Cresotic acid (5 grams), chloral hydrate (5 grams), and sulphuric acid (50 c.c. of 94—95 per cent.) were mixed together, when the solids dissolved easily. After three days, the solution was poured on ice, when a white solid separated, which was collected, washed with water, and dried on a porous tile; the yield of the crude product was 7 grams. It was sparingly soluble in most organic solvents, and separated from glacial acetic acid as a white, microcrystalline powder melting and decomposing at 283—285° (the melting point being determined quickly) (Found: Cl = 24·32. $C_{18}H_{15}O_6Cl_3$ requires Cl = 24·55 per cent.).

The *calcium* salt was prepared (Found: Ca = 8·3. $C_{18}H_{13}O_6Cl_3Ca$ requires Ca = 8·5 per cent.).

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XXIV.—*Studies in Substituted Quaternary Azonium Compounds containing an Asymmetric Nitrogen Atom. Part IV. Additive Compounds of Thiocarbamide with Azonium Iodides.*

By Bawa Kartar Singh and Mibi Lal.

The object of this investigation was to determine the ratio in which thiocarbamide unites directly with substituted quaternary azonium iodides of different constitution.

Werner and Atkins (T., 1912, **101**, 1988) found that whilst the simplest ammonium bases and primary amines form tetrathiocarbamide derivatives, the tertiary amines and quaternary ammonium bases appear always to produce dithiocarbamide compounds.

The substituted quaternary azonium iodides also form dithiocarbamide derivatives, thus resembling the quaternary ammonium compounds in their capacity to yield additive compounds with thiocarbamide.

Exceptions to the above rule are found in phenylbenzylallylazonium iodide, which forms a monothiocarbamide compound, and the phenyldimethyl and phenyldiethyl compounds, which do not unite at all with thiocarbamide.

The thiocarbamide additive compounds described below have comparatively high melting points, which seems to imply increased stability of both thiocarbamide and azonium iodides in these substances. The azonium iodides have comparatively low decomposition temperatures.

Experimental.

Preparation of Additive Compounds of Thiocarbamide and Azonium Iodides.

The general method adopted at first in the preparation of these compounds consisted in mixing hot alcoholic solutions of thiocarbamide and azonium iodides. On cooling, the additive compound separated, and was purified by recrystallisation from alcohol. Better yields and purer products, however, were obtained by heating a concentrated alcoholic solution of the components containing an excess of thiocarbamide. The solution was cooled and then filtered. To the filtrate, alcohol-free, dry ether was added, which precipitated the compound.

The azonium iodides used were prepared and purified according to methods already described (Singh, T., 1913, **103**, 604; 1914, **105**, 1972; 1920, **117**, 1202).

The results obtained are given below.

Thiocarbamide and Phenylmethylethylazonium Iodide.—This compound forms fine, silky needles melting at 192—193° (Found: I = 30·24, 29·7. $PhMeEt[NH_2]NI,2CH_4N_2S$ requires I = 29·54 per cent.).

Thiocarbamide and Phenylbenzylmethylazonium Iodide.—The additive compound was obtained as a white, crystalline substance melting at 211° (Found: I = 25·68, 26·06.

$$Ph[CH_2Ph]Me[NH_2]NI,2CH_4N_2S$$

requires I = 25·81 per cent.).

Thiocarbamide and Phenylbenzylpropylazonium Iodide.—The double compound was obtained as a white, crystalline substance melting at 180—181° (Found: I = 24·72, 24·28.

$$Ph[CH_2Ph]Pr[NH_2]NI,2CH_4N_2S$$

requires I = 24·42 per cent.).

Thiocarbamide and Phenylbenzylallylazonium Iodide.—This compound forms fine, silky needles melting at 187—188° (Found: I = 28·41. $Ph[CH_2Ph][C_3H_5][NH_2]NI,CH_4N_2S$ requires I = 28·73 per cent.).

It is noteworthy that phenyldimethylazonium iodide and phenyldiethylazonium iodide do not give any compounds with thiocarbamide, though in each case the azonium iodide was boiled with varying proportions of thiocarbamide in alcoholic solution. This may be due to the presence of two like alkyl radicles in the azonium iodides. Werner and Atkins (*loc. cit.*) also found that tetramethylammonium iodide does not exhibit any tendency to unite with thiocarbamide.

The iodine was estimated in all the above compounds by boiling with an excess of iron alum and dilute sulphuric acid, and titrating the liberated iodine with a standard solution of sodium thiosulphate.

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[*Received, January 20th, 1921.*]

XXV.—*Condensation of* p-*Nitrobenzyl Chloride with Nitroso-compounds. A New Mode of Formation of* N-*Oximino-ethers.*

By Fred Barrow and Evan Dalton Griffiths.

During the course of an investigation on the action of alcoholic potassium hydroxide on *p*-nitrobenzylidene chloride, it was found by one of us that this substance and *p*-nitrobenzyl chloride readily undergo condensation with aromatic aldehydes, under the influence of the condensing agent, with the formation of derivatives of stilbene oxide. Thus, for example, *p*-nitrobenzylidene chloride condenses with *p*-nitrobenzaldehyde, yielding α-chloro-*pp'*-dinitrostilbene oxide (I), whilst *p*-nitrobenzyl chloride gives rise to two stereoisomeric, *cis*- and *trans*-, *pp'*-dinitrostilbene oxides (II).

$$\left.\begin{array}{l}NO_2\cdot C_6H_4\cdot CCl\\ NO_2\cdot C_6H_4\cdot CH\end{array}\right>O \qquad \left.\begin{array}{l}NO_2\cdot C_6H_4\cdot CH\\ NO_2\cdot C_6H_4\cdot CH\end{array}\right>O$$

(I.) (II.)

In view of the remarkable ease with which these condensations take place, a study of the behaviour of the nitro-substituted benzylidene and benzyl chlorides towards other classes of compounds containing an unsaturated group is being undertaken by the authors, and in the present communication the interaction of *p*-nitrobenzyl chloride with aromatic nitroso-compounds is described. It has been found that nitrosobenzene, and also the *p*-nitroso-derivatives of the mono- and di-alkylanilines, readily condense with *p*-nitrobenzyl chloride in the presence of alcoholic potassium hydroxide, yielding *N*-aryl ethers of *p*-nitrobenzaldoxime, thus:

$$NO_2\cdot C_6H_4\cdot CH_2Cl + NPh\colon O = HCl + NO_2\cdot C_6H_4\cdot CH\colon NPh\colon O.$$

The constitution of these condensation products was first established by the investigation of the behaviour of the *N*-phenyl ether prepared from *p*-nitrobenzyl chloride and nitrosobenzene, towards hydrochloric acid. When heated with concentrated hydrochloric acid, the phenyl ether is rapidly hydrolysed to *p*-nitrobenzaldehyde and *p*-chloroaniline. The initial products of the hydrolysis evidently consist of the aldehyde and β-phenylhydroxylamine, the latter compound being subsequently converted into *p*-chloroaniline by the further action of the hydrochloric acid:

$$NO_2\cdot C_6H_4\cdot CH\colon NPh\colon O \longrightarrow NO_2\cdot C_6H_4\cdot CHO + C_6H_5\cdot NH\cdot OH \longrightarrow C_6H_4Cl\cdot NH_2.$$

Further evidence as to the constitution of these condensation products is furnished by the direct synthesis of the *N*-phenyl ether, by the interaction of *β*-phenylhydroxylamine and *p*-nitrobenzaldehyde in alcoholic solution:

$$NO_2{\cdot}C_6H_4{\cdot}CHO + NHPh{\cdot}OH \longrightarrow H_2O + NO_2{\cdot}C_6H_4{\cdot}CH{:}NPh{:}O.$$

It has been shown by Semper and Lichtenstadt (*Ber.*, 1918, **51**, 928) that the *N*-methyl ether of phenyl *p*-tolyl ketoxime exists in two stereoisomeric forms, corresponding with the *syn*- and *anti*-modifications of the oxime.

In view of the existence of these isomerides, and also of the simultaneous formation of *cis*- and *trans*-*pp'*-dinitrostilbene oxides by the condensation of *p*-nitrobenzyl chloride with *p*-nitrobenzaldehyde, the crude *N*-*p*-dimethylaminophenyl ether, prepared from *p*-nitrobenzyl chloride and *p*-nitrosodimethylaniline, was submitted to a careful fractional crystallisation from alcohol in order to ascertain whether stereoisomeric ethers are formed in this condensation, but no evidence of the existence of a second isomeride was obtained.

The interaction of *p*-nitrobenzyl chloride with nitroso-compounds is analogous to that of the aliphatic diazo-compounds described by Staudinger and Miescher (*Helv. Chim. Acta*, 1919, **2**, 554), who have shown that diazo-compounds of the type $\begin{matrix}N\\ \|\\ N\end{matrix}\!\!>C<\!\begin{matrix}R\\ R'\end{matrix}$ readily react with nitrosobenzene and its derivatives, yielding *N*-oximino-ethers.

Attempts to condense *p*-nitrobenzyl chloride with nitrosoamines, $NRR'{\cdot}NO$, were unsuccessful, the nitrosoamine being recovered unchanged, whilst the *p*-nitrobenzyl chloride was converted by the alcoholic potassium hydroxide into *pp'*-dinitrostilbene.

The reaction described in the present communication is being extended to other nitro-derivatives of benzyl chloride. It has also been found that aromatic chloro-ketones of the types $CH_2Cl{\cdot}COR$ and $CHRCl{\cdot}COR$ react with nitroso-compounds, yielding *N*-oximino-ethers.

EXPERIMENTAL.

p-*Nitrobenzaldoxime*-N-*phenyl Ether*, $NO_2{\cdot}C_6H_4{\cdot}CH{:}NPh{:}O$.

Equimolecular proportions of *p*-nitrobenzyl chloride (8·6 grams) and nitrosobenzene (5·4 grams) were dissolved in the minimum amount of alcohol at the ordinary temperature, and the solution treated with one and a-half times the theoretical amount of potassium hydroxide (4·2 grams) dissolved in methyl alcohol

(30 c.c.). On the addition of the alkali, the colour of the solution rapidly changed from green to light reddish-brown, and the oximino-ether separated in the form of a yellow, crystalline powder. After remaining for one hour at the ordinary temperature, this was filtered, freed from potassium chloride by washing with water, and crystallised from alcohol.

p-*Nitrobenzaldoxime*-N-*phenyl ether* crystallises in small, slender, pale yellow leaflets, which melt at 182° (Found: C=64·46; H=4·29; N=11·50. $C_{13}H_{10}O_3N_2$ requires C=64·46; H=4·13; N=11·57 per cent.). It is very readily soluble in chloroform, moderately so in alcohol and benzene, and almost insoluble in ether and light petroleum.

Hydrolysis.—The *N*-phenyl ether (4 grams) was heated for half an hour with concentrated hydrochloric acid (30 c.c.), and, after cooling, the solid which separated was purified by crystallisation from dilute alcohol, and then from water. It crystallised in almost colourless needles melting at 106°, and was identified as *p*-nitrobenzaldehyde. The acid solution, from which the *p*-nitrobenzaldehyde separated, was extracted with ether, and then rendered alkaline by the addition of sodium hydroxide. The base thus liberated gave with acetic anhydride an acetyl derivative melting at 175°, which was identified as *p*-chloroacetanilide.

Condensation of p-*Nitrobenzaldehyde and β-Phenylhydroxylamine.*

For the purpose of comparison, *p*-nitrobenzaldoxime-*N*-phenyl ether was prepared by the condensation of *p*-nitrobenzaldehyde and β-phenylhydroxylamine.

Equimolecular proportions of the two components were separately dissolved in alcohol, and, after mixing, the solution was heated for half an hour on the water-bath. The solid which separated crystallised from alcohol in pale yellow leaflets melting at 182°, and was identical with the *N*-phenyl ether obtained by the condensation of *p*-nitrobenzyl chloride and nitrosobenzene.

p-*Nitrobenzaldoxime*-N-p-*dimethylaminophenyl Ether*,
$NO_2 \cdot C_6H_4 \cdot CH\!:\!NO \cdot C_6H_4 \cdot NMe_2$.

28·6 Grams of *p*-nitrobenzyl chloride and 25 grams of *p*-nitrosodimethylaniline were dissolved in the minimum amount of alcohol at the ordinary temperature, and to the solution was added the theoretical amount of potassium hydroxide (9·3 grams) dissolved in methyl alcohol (66 c.c.). On the addition of the alkali, the colour of the solution rapidly changed from green to dark choco-

late-red, and the oximino-ether separated in the form of a brownish-red powder. After one hour, this was filtered, washed with water, and purified by crystallisation from a mixture of equal parts of pyridine and alcohol, the yield being 33·5 grams.

The N-p-*dimethylaminophenyl ether* crystallises in chocolate-red needles melting at 201°, and forms a yellow hydrochloride and sulphate (Found: C = 63·09; H = 5·20; N = 14·58. $C_{15}H_{15}O_3N_3$ requires C = 63·15; H = 5·26; N = 14·74 per cent.). It is readily soluble in chloroform and pyridine, sparingly so in benzene and alcohol, and practically insoluble in light petroleum and ether. When heated with concentrated hydrochloric acid, it readily undergoes hydrolysis, with the formation of *p*-nitrobenzaldehyde.

p-*Nitrobenzaldoxime*-N-p-*diethylaminophenyl Ether*, $NO_2·C_6H_4·CH\!:\!NO·C_6H_4·NEt_2$.

This was prepared from *p*-nitrosodiethylaniline and *p*-nitrobenzyl chloride in a similar manner to that described above, and purified by crystallisation from a mixture of equal parts of pyridine and alcohol. It crystallises in large, lustrous, bright crimson leaflets, which melt at 167°, is readily soluble in pyridine and chloroform, but only sparingly so in alcohol and benzene (Found: C = 64·99; H = 6·01; N = 13·34. $C_{17}H_{19}O_3N_3$ requires C = 65·17; H = 6·07; N = 13·42 per cent.).

p-*Nitrobenzaldoxime*-N-p-*di*-n-*propylaminophenyl Ether*, $NO_2·C_6H_4·CH\!:\!NO·C_6H_4·NPr^{a}_2$.

This compound is obtained in a similar manner from *p*-nitrosodi-n-propylaniline, and separates from alcohol in felted, slender, dark crimson needles melting at 135—138° with previous softening at 130° (Found: N = 12·31. $C_{19}H_{23}O_3N_3$ requires N = 12·32 per cent.). It is much more readily soluble in the common solvents than the dimethylaminophenyl ether.

p-*Nitrobenzaldoxime*-N-p-*ethylaminophenyl Ether*, $NO_2·C_6H_4·CH\!:\!NO·C_6H_4·NHEt$.

The condensation of *p*-nitrosoethylaniline, prepared by Fischer and Hepp's method (*Ber.*, 1886, **19**, 2993), with *p*-nitrobenzyl chloride was carried out at 45°, the reaction proceeding only slowly at the ordinary temperature.

The p-*ethylaminophenyl ether* crystallises from benzene in deep crimson needles melting at 168° (Found: C = 63·08; H = 5·25; N = 14·53. $C_{15}H_{15}O_3N_3$ requires C = 63·15; H = 5·26; N = 14·74

per cent.). It is readily soluble in alcohol and chloroform, less so in benzene, and only very sparingly so in ether and light petroleum.

p-*Nitrobenzaldoxime*-N-p-*nitrophenyl Ether*, $NO_2\cdot C_6H_4\cdot CH\colon NO\cdot C_6H_4\cdot NO_2$.

The *p*-nitronitrosobenzene required for the preparation of this compound was obtained by the addition of the calculated amount of Caro's acid to a well-cooled solution of *p*-nitroaniline in concentrated sulphuric acid, and was separated from the accompanying *p*-dinitrobenzene by fractional distillation in steam (compare Bamberger, *Ber.*, 1903, **36**, 3808). The product resulting from the condensation of the nitroso-compound with *p*-nitrobenzyl chloride consisted of a mixture of the oximino-ether and *pp'*-dinitrostilbene, which was readily separated by taking advantage of the sparing solubility of the latter compound in alcohol.

The p-*nitrophenyl ether* separates from alcohol in the form of a pale yellow, crystalline powder, which melts at 186° (Found: N = 14·54. $C_{13}H_9O_5N_3$ requires 14·63 per cent.). It is readily soluble in chloroform, moderately so in alcohol and benzene, and insoluble in ether and light petroleum.

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[*Received, January 27th*, 1921.]

XXVI.—*The Oxidation of Carbazole.*

By William Henry Perkin, jun., and Stanley Horwood Tucker.

Fission of the rings of carbazole by oxidation methods has been attempted by several investigators. Graebe and Glaser (*Ber.*, 1872, **5**, 12) found that chromic acid in glacial acetic acid solution reacted very vigorously with carbazole, but the product isolated from the reaction mixture contained chromium, and was not identifiable. It is noteworthy that Branch and Smith (*J. Amer. Chem. Soc.*, 1920, **42**, 2405) * obtained, by the oxidation of carb-

* The results contained in the following communication were reported to the Department of Scientific and Industrial Research in October, 1919. The above-mentioned paper by Branch and Smith made it advisable to publish an account of our experiments, although they are at present somewhat incomplete.

azole with silver oxide in benzene solution, a product which contained silver.

The only instance of ring-rupture in the carbazole molecule is that recorded by Padoa and Chiaves (*Atti. R. Accad. Lincei*, 1908, [v], **16**, ii, 762), who found that 2:3-diethylindole is produced by heating carbazole with nickel in an atmosphere of hydrogen under pressure.

Wieland and Gambarjan (*Ber.*, 1906, **39**, 1506) stated that carbazole was unaffected by shaking in benzene solution with lead peroxide, and also that a cold 3 per cent. solution of potassium permanganate in acetone had similarly no action on carbazole.

We find, however, that when finely divided potassium permanganate is added to a hot solution of carbazole in pure acetone, a vigorous reaction sets in, and from the reaction mixture three products have been isolated: two well-defined, crystalline compounds melting, respectively, at 220—221° and 265°, and an amorphous substance. The amorphous substance, which is the main product of the oxidation, has not yet been analysed. It is evidently of high molecular weight, since it cannot be distilled. The two crystalline compounds, which we distinguish provisionally as (*A*) and (*B*), both possess the formula $C_{24}H_{16}N_2$, and are undoubtedly isomeric *dicarbazyls*, analyses and molecular-weight determinations by the cryoscopic method in the solvents benzene and naphthalene being in complete support of this formula.

There is no indication at present that either a benzene ring or the pyrrole ring of the carbazole molecule can be opened by oxidation methods. During our oxidation experiments, carried out on a large scale, no amino-acids could be detected by means of the copper or lead salts.

Dicarbazyl (*A*), m. p. 220—221°, crystallises from benzene in large crystals, which evidently contain benzene of crystallisation, and these, when exposed to the air, fall to powder. It crystallises particularly well from acetone, and the measurement of the crystals thus obtained is described on p. 222.

Dicarbazyl (*B*), m. p. 265°, crystallises from a mixture of acetone and benzene in minute, glistening crystals, which are not suitable for measurement.

Carbazole fused with anhydrous oxalic acid gives a melt which is first green and finally becomes blue. This "carbazole-blue" test, when applied to dicarbazyl (*A*), of melting point 220°, gives a distinctly green melt, which turns blue; but the isomeride (*B*), melting at 265°, gives only a faintly blue melt, different in tint from the above.

It is remarkable that neither of these two substances forms a

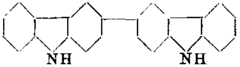
picrate, for carbazole and its homologues combine readily with picric acid.

The behaviours of the dicarbazyls (*A*) and (*B*) towards concentrated sulphuric acid are characteristic, and different from that given by carbazole. Both react with nitric acid to give yellow nitro-derivatives, and are violently attacked by bromine.

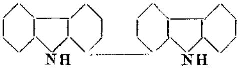
Three possible types of isomeric dicarbazyls may be distinguished, namely:

(1) *NN*-Dicarbazyl, in which the linking of the carbazyl radicles is effected through nitrogen. There is only one possibility in this case, namely, the hydrazine formula,

(2) *CC*-Dicarbazyls, in which the union of the carbazyl radicles is attained through carbon. In this class there are several possible modes of linking, but the two most probable are represented by (I) and (II), since in the carbazole molecule the hydrogen atoms



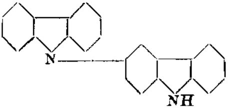
3 : 3′-Dicarbazyl.
(I.)



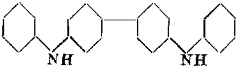
1 : 1′-Dicarbazyl.
(II.)

in the positions 3 and 1 are the most reactive, and hydrogen in position 3 is more reactive than hydrogen in position 1.

(3) *CN*-Dicarbazyls, in which the carbon of one carbazyl radicle is linked to the nitrogen of the other, for example, formula (III).



(III.)



(IV.)

Relevant to the discussion of the constitution of the dicarbazyls is the observation of Wieland (*Ber.*, 1913, **46**, 3300) that, by the oxidation of diphenylamine with sodium dichromate in glacial acetic acid solution in the presence of sulphuric acid, diphenylbenzidine (IV) is obtained.

The behaviour of carbazole under these conditions is being investigated.

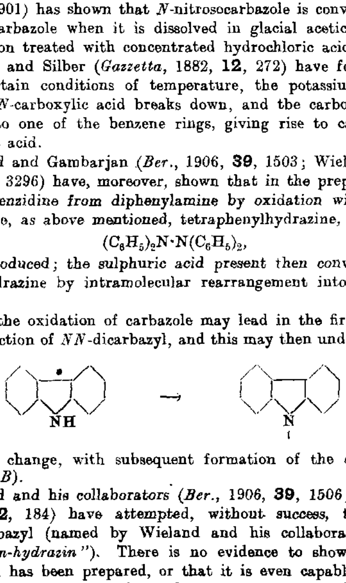
It is probable that the two modifications of dicarbazyl obtained under the conditions described in this research are not the first products of the oxidation of carbazole. It is well known that the hydrogen atoms in positions 1 and 3 in carbazole are particularly susceptible to substitution, and several instances of wandering to these positions of groups attached to the nitrogen atom of the *imide group* have been observed. Thus, H. Schott (D.R.-P. 134983, 1901) has shown that *N*-nitrosocarbazole is converted into 3-nitrosocarbazole when it is dissolved in glacial acetic acid and the solution treated with concentrated hydrochloric acid. Again, Ciamician and Silber (*Gazzetta*, 1882, **12**, 272) have found that, under certain conditions of temperature, the potassium salt of carbazole-*N*-carboxylic acid breaks down, and the carboxyl group wanders to one of the benzene rings, giving rise to carbazole-1-carboxylic acid.

Wieland and Gambarjan (*Ber.*, 1906, **39**, 1503; Wieland, *Ber.*, 1913, **46**, 3296) have, moreover, shown that in the preparation of diphenylbenzidine from diphenylamine by oxidation with sodium dichromate, as above mentioned, tetraphenylhydrazine,

$$(C_6H_5)_2N\cdot N(C_6H_5)_2,$$

is first produced; the sulphuric acid present then converts tetraphenylhydrazine by intramolecular rearrangement into diphenylbenzidine.

Hence the oxidation of carbazole may lead in the first place to the production of *NN*-dicarbazyl, and this may then undergo intra-



molecular change, with subsequent formation of the dicarbazyls (*A*) and (*B*).

Wieland and his collaborators (*Ber.*, 1906, **39**, 1506; *Annalen*, 1912, **392**, 184) have attempted, without success, to prepare *NN*-dicarbazyl (named by Wieland and his collaborators "*bis-diphenylen-hydrazin*"). There is no evidence to show that this compound has been prepared, or that it is even capable of existence; nor is there any evidence that any dicarbazyl had been prepared before the publication of the present investigation.

At the present stage of this research, it is not possible to say to which type or types the two crystalline dicarbazyls which we have isolated belong, except that one of them must belong to type II or III. With the object of testing whether either compound was the hydrazine, attempts were made to reduce these two

substances, but without success. It was to be expected that the hydrazine, *NN*-dicarbazyl, would readily reduce to carbazole. Practical exigencies, for example, sparing solubility of these two compounds in alcohol, glacial acetic acid, and other solvents, have given rise to difficult experimental conditions, and the question is being further investigated.

Attempts to acetylate the two crystalline dicarbazyls (*A*) and (*B*) have met with only partial success. Both compounds crystallise unchanged from acetic anhydride, but when boiled with excess of anhydride in the presence of a catalyst (for example, a trace of concentrated sulphuric acid, zinc chloride, potassium hydrogen sulphate, etc.), the solution darkens, and, on addition of water, substances are precipitated which are in part soluble in hot alcohol. The investigation of these alcohol-soluble products is in progress. Acetyl chloride and benzoyl chloride appear to have merely a solvent action, but this behaviour cannot be taken as proof of the absence of the imide group in these dicarbazyls, since carbazole itself reacts only imperfectly with these reagents.

EXPERIMENTAL.

Oxidation of Carbazole with Potassium Permanganate in Acetone Solution.—To a boiling solution of 100 grams of carbazole in 700 grams of pure acetone are added 100 grams of finely powdered potassium permanganate in two portions of 50 grams each. [The acetone was purified by boiling with excess of potassium permanganate until the purple colour persisted, and was then distilled from the mixture.] On addition of the first 50 grams, a vigorous reaction sets in, and continues for about three to five minutes; the permanganate colour will then have practically disappeared. The remaining 50 grams of potassium permanganate are now added to the acetone solution, and the whole boiled vigorously on the water-bath, with occasional shaking, until the pink colour is discharged, which is the case in about one hour. After filtering from the brown manganese precipitate, the faintly pink filtrate commences at once to deposit a small quantity of a white, pasty precipitate, which soon becomes crystalline. The manganese precipitate is washed with hot acetone, the residue is returned to the flask, and extracted twice with boiling acetone (about 400 grams each time). The united acetone filtrates, which exhibit a deep violet fluorescence, are now evaporated.

The manganese precipitate was extracted twice with benzene, but yielded only 1—2 grams of syrup, and this was added to the acetone extract. In order to determine whether any other sub-

tances, such as amino-acids, had been formed during the oxidation, the residue in one case was extracted several times with boiling water until the filtrate was nearly neutral. The united filtrates were rendered slightly acid with acetic acid, the liquid heated to boiling, filtered from a slight amount of a dirty brown precipitate, and solutions of copper acetate and of lead acetate added to portions of the filtrate, but no copper or lead salts of organic acids separated.

Some of the manganese residue was mixed into a paste with water, and sulphur dioxide gas passed until the manganese had dissolved, but only a slight amount of a dirty brown precipitate separated.

Examination of the Acetone Extract.—The brown oxidation mass, obtained as described above, which weighs 110 grams, is dissolved in boiling benzene. The deep red-coloured liquid, which exhibits a violet fluorescence, deposits white crystals on keeping. These are washed with a little cold benzene. The crystals melt at 210°, with evidence of softening at 200°, and weigh 24 grams. This substance (called dicarbazyl *A*) is first recrystallised from benzene, and finally twice from acetone, and is thus obtained in large crystals (20 grams) melting at 220—221° (224—225° corr.).

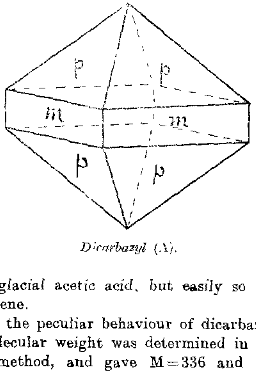
The combined mother liquors of dicarbazyl (*A*) are mixed with twice the volume of acetone, and the solution so obtained is allowed to remain several days. A white, microcrystalline substance (dicarbazyl *B*), about 5 grams, gradually separates, and melts at about 252°, but after recrystallisation at 265° (270° corr.). From the acetone–benzene filtrate the excess of acetone is distilled off, and to the residual liquor sufficient alcohol (97 per cent.) is added to cause a slight precipitation. The mixture is then poured into warm alcohol, when a pink, pasty mass separates, which, on stirring vigorously, disintegrates into a faintly pink, flocculent substance. The suspension in alcohol is allowed to remain twenty-four hours, collected, ground up with a further quantity of alcohol, again collected, and washed. The dried mass weighs 70—75 grams, and melts at about 175—200°, and is conveniently designated (*C*).

All efforts to improve the yields of the two crystalline products have been unavailing. The use of a smaller quantity of acetone causes the potassium permanganate to cake and become coated with manganese oxides. On the other hand, the addition of larger quantities of acetone has no beneficial result. The employment of a larger quantity of permanganate also does not improve the yield, whilst if a less amount is used, unchanged carbazole remains.

Examination of Dicarbazyl (A), *melting at* 220—221°.—

This substance separates from benzene in fine, large crystals, but when these are removed from the solution and exposed to the air, they at once commence to become opaque at the ordinary temperature, and do so more rapidly in the steam-oven, falling to a white powder. The melting point is unaltered by this change, which indicates that dicarbazyl (*A*) crystallises with benzene of crystallisation. Apparently the substance crystallises from toluene and xylene without added solvent (Found: C=86·7; H=4·9; N=8·4. $C_{24}H_{16}N_2$ requires C=86·7; H=4·8; N=8·4 per cent.).

Dicarbazyl (*A*) is soluble in acetone, but not as easily as in the other solvents just mentioned. The solution in acetone exhibits a pale violet fluorescence, and deposits large crystals possessing a faint, steel-blue tint. It is soluble with difficulty in



Dicarbazyl (A).

alcohol and in glacial acetic acid, but easily so in nitrobenzene and in naphthalene.

On account of the peculiar behaviour of dicarbazyl (*A*) towards benzene, the molecular weight was determined in naphthalene by the cryoscopic method, and gave M=336 and 327. $C_{24}H_{16}N_2$ requires M=332.

The crystallographic examination of dicarbazyl (*A*), melting at 220—221°, was kindly carried out by Miss M. W. Porter, with the following result:

The crystals from acetone are orthorhombic, and show the following two forms: *m*{110}, *p*{111}. The habit is pyramidal, as shown in the figure.

The mean results of measurement for *m*{110} are: azimuth (ϕ)=60°2′, polar distance (ρ)=90°0′; for *p*{111}: azimuth

$(\phi)=60°1'$, polar distance $(\rho)=55°11'$. Axial ratios: $a:b:c=$ 0·5766 : 1 : 0·7182.

Several attempts were made to acetylate dicarbazyl (*A*), for example, by dissolving the substance (0·5 gram) in acetic anhydride (4 c.c.) and boiling the solution for one hour. On cooling, large crystals of unchanged substance (m. p. 219—220°) separated, and on pouring the acetic anhydride filtrate into water there was no further precipitate.

Again, separate portions of 0·5 gram of substance were dissolved in 4 c.c. of acetic anhydride, and to these solutions were added (1) a drop of concentrated sulphuric acid, (2) 0·1 gram of fused potassium hydrogen sulphate, and (3) 0·1 gram of fused zinc chloride, and the solution was in each case boiled for one hour. The solutions in experiments (1) and (3) darkened, but (2) remained colourless, so the boiling was continued in this experiment for another two hours. No crystalline matter separated from the solutions on keeping, but when poured into water, (1) and (3) gave a pink solid and a considerable amount of iridescent scales. The addition of water to (2) brought about the precipitation of a white solid possessing a silky sheen. These precipitates were soluble in alcohol, but were quite indefinite, and all attempts to isolate any satisfactory product from any of them were unsuccessful.

Dicarbazyl (*A*) dissolves in cold concentrated sulphuric acid to an emerald-green solution, which, on warming, turns dirty green, but addition of a drop of concentrated nitric acid to the solution in sulphuric acid turns the colour to a deep blue.

The solution in toluene, treated with concentrated nitric acid in the cold and allowed to remain, deposits yellow crystals, which do not melt at 330°.

Bromine reacts violently with dicarbazyl (*A*), as it does with carbazole, but the products have not yet been investigated.

When fused with anhydrous oxalic acid, dicarbazyl (*A*) yields a deep green melt, which finally turns blue.

No picrate could be obtained by treating either the benzene, acetone, or alcoholic solution of dicarbazyl (*A*) with picric acid.

If carefully heated, dicarbazyl (*A*) melts without decomposition, but finally chars, and gives a white sublimate different in appearance from the fluffy sublimate of carbazole.

Examination of the Dicarbazyl (B) *melting at* 265°.—Some difficulty was experienced in the isolation of this substance from the crude material melting at 252° (see p. 221), but a pure product was obtained by dissolving the crude substance in hot benzene,

pouring into twice the volume of cold acetone, and allowing to remain until the fine, crystalline deposit had completely separated. Several repetitions of this process, followed by a crystallisation from acetone, in which the substance is only slightly soluble, gave small, bright, white crystals melting, without preliminary browning, at 265° (270° corr.) to a clear, yellow melt, which almost immediately blackens.

Subsequently, in an attempt to acetylate this dicarbazyl (*B*) by boiling with acetic anhydride, it was found that it crystallises well from this reagent, and the melting point may be raised in this way to 268° (273° corr.). Dicarbazyl (*B*) also crystallises from nitrobenzene, aniline, pyridine, toluene, and xylene (Found: *C*=86·7; H=4·8; N=8·1. The molecular weight by the cryoscopic method in benzene gave M=330. $C_{24}H_{16}N_2$ requires C=86·7; H=4·8; N=8·4 per cent. Molecular weight=332.).

Attempts to acetylate dicarbazyl (*B*) under a variety of conditions gave results very similar to those obtained in the case of dicarbazyl (*A*), and no definite product could be isolated in any case.

Dicarbazyl (*B*) is insoluble in cold concentrated sulphuric acid, but, on warming, dissolves with a dull green colour, unaffected by the addition of a drop of concentrated nitric acid.

Bromine reacts violently with the substance. Fusion of the substance (*B*) with anhydrous oxalic acid gives a faintly blue melt, different in tint from that of carbazole-blue.

Attempts to prepare a picrate were unsuccessful.

The Amorphous Substance (C).—All attempts to crystallise the flocculent, faintly pink material precipitated by addition of alcohol to the benzene filtrates of (*A*) and (*B*), as explained on p. 221, have proved futile. By several repetitions of this process, or by the addition of alcohol to the ethereal solution, a cream-coloured, amorphous powder having a peculiar silky sheen is obtained, but the amount is small.

The substance (*C*) is very soluble to red-coloured solutions in benzene, toluene, pyridine, chloroform, and in hot ethyl acetate; it is also somewhat soluble in hot methyl and ethyl alcohols, glacial acetic acid, acetic anhydride, aniline, and ether, less so in acetone, light petroleum, and in amyl alcohol; it is insoluble in dilute sodium hydroxide, ammonium hydroxide, and concentrated hydrochloric acid solutions. The substance (*C*) is precipitated from its solutions by alcohol, water, and by acetic acid. Crystallisation could not be effected from any of these solvents or from mixtures of them. Soxhlet extraction experiments, using acetone, glacial acetic acid, and methyl alcohol, failed to separate any constituent other than traces of the dicarbazyls (*A*) and (*B*).

As (*C*) could not be obtained in a sufficiently definite crystalline condition, no further work has in the meantime been done with it. It dissolves in concentrated sulphuric acid with a green colour, and does not give a picrate. The substance reacts violently with bromine and readily with nitric acid to give yellow derivatives.

Summary.

By the action of potassium permanganate on carbazole in boiling acetone solution, three substances are produced: two crystalline compounds, melting at 220—221° and at 265° respectively, and an amorphous substance. The two crystalline compounds are isomeric dicarbazyls, and combustion analyses and molecular weight determinations in naphthalene and in benzene show that they have the molecular formula $C_{24}H_{16}N_2$.

All three substances can be nitrated and brominated, and react under certain conditions with acetic anhydride. They do not form picrates.

The authors desire to express their indebtedness to the Department of Scientific and Industrial Research for a grant which has enabled this research to be carried out, and also wish to thank Miss M. W. Porter and Mr. T. V. Barker for the crystallographic measurements contained in this paper.

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[*Received, January* 21*st*, 1921.]

XXVII.—*The Influence of Mercury, Sulphur, Arsenic, and Zinc on the Catalytic Activity of Platinum.*

By EDWARD BRADFORD MAXTED.

IN a previous communication (T., 1920, **117**, 1501), it has been shown that the inhibitive effect of varied proportions of lead on the catalytic activity of platinum is, within certain limits, directly proportional to the concentration of the inhibitant. In view of this result, and with the object of examining the general applicability and limits of a linear poisoning law, the work has now been extended to other inhibitants.

In order to eliminate the necessity of obtaining the value representing the activity of the catalyst from the equation to the absorption curve by a process of differentiation, great care has been given

to the purity of all materials employed for the measurements. Absorption curves were thus obtained of the form which Armstrong and Hilditch (*Proc. Roy. Soc.*, 1919, [*A*], **96**, 137, 322) have recently shown to be typical of pure substances, this form being found also to be unaltered by the presence of inhibitants of the type studied. From these curves, the catalytic activity of the preparation could be read off directly without recourse to mathematical treatment. The conditions have thus been rendered more precise, and it has been possible to plot with considerable accuracy the form and limits of the poisoning curves.

As before, the variation of the catalytic activity of the platinum has been followed by measuring its activity when employed for catalytic hydrogenation under standard conditions. In general, the existence of a linear poisoning law has been confirmed. The limits between which this holds would appear to be from a zero concentration of inhibitant up to a region in the neighbourhood of total extinction, where a point of inflexion occurs, from which the poisoning curve slopes far less steeply towards complete inactivity. The existence of this small residual activity, which is thus more resistant to the action of poisons than the main portion of the original activity possessed by the catalyst, is of considerable theoretical interest, and renders the poisoning curve somewhat analogous in form to that of the absorption curves themselves, in which the predominating linear portion is followed by a point of inflexion and a sudden decrease in the rate of absorption of gas.

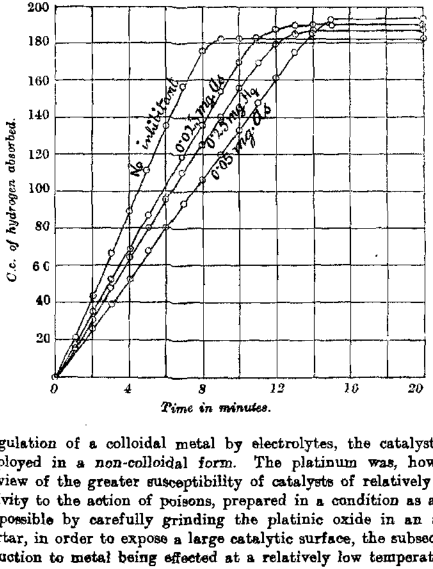
EXPERIMENTAL.

The oleic acid, which was employed as a standard, unsaturated substance for measuring the catalytic activity of the various preparations, was, owing to difficulties in obtaining supplies of acid of sufficient purity, prepared by shaking purest commercial olive oil with hot distilled water containing a small quantity of sodium hydroxide, as in the usual procedure for refining oils by means of alkali. The aqueous phase was rejected, and, after frequent washing with boiling water, the oil was dried and treated at 100° with fuller's earth, the latter treatment being repeated several times. Hydrolysis was next effected in the usual manner by means of sodium hydroxide in dilute alcoholic solution, and the almost completely colourless, fatty acid obtained was, after renewed washing with boiling water and subsequent drying in a current of nitrogen, found to be sufficiently free from impurities to give an absorption curve of the form described. In view of the requirements merely for a homogeneous, "catalytically pure,"

unsaturated substance, it was not considered necessary to eliminate, by subsequent treatment, the small quantities of homologues of oleic acid which are present in olive oil, and consequently in the oleic acid obtained.

It was found possible to obtain both platinic oxide and glacial acetic acid of sufficient purity, the properties of the solvent being found to be practically unaffected, from a catalytic point of view, by subsequent purification in the laboratory.

In order to avoid the possibility of complications due to the



coagulation of a colloidal metal by electrolytes, the catalyst was employed in a *non-colloidal* form. The platinum was, however, in view of the greater susceptibility of catalysts of relatively high activity to the action of poisons, prepared in a condition as active as possible by carefully grinding the platinic oxide in an agate mortar, in order to expose a large catalytic surface, the subsequent reduction to metal being effected at a relatively low temperature.

Form of the Absorption Curve.

Previous to the recent work of Armstrong and Hilditch (*loc. cit.*), the course of the catalytic hydrogenation of liquids in the

presence of unpoisoned catalysts had been supposed to follow the unimolecular law, any deviation from this being attributed to the presence of impurities. These investigators have shown that, with increasing purity of the reacting substances, absorption of hydrogen takes place more rapidly than is required by a unimolecular reaction, and that the true form for reactants in a state of purity is that to which reference has already been made.

The present measurements, in the absence of catalyst poisons, confirm Armstrong and Hilditch's observations, and the general form of the reaction curve would appear also to be unaffected by the presence of inhibitants of the nature studied, this being, however, not the case with "clogging" poisons, probably of an albuminoid or resinous nature, such as are found in oils and other organic liquids of ordinary purity. The independence of the form of the reaction curve on the presence of catalyst poisons of the first class is illustrated by the results collected in the figure, which summarises the course of the absorption of hydrogen by a system consisting of 3 c.c. of oleic acid, dissolved in 9 c.c. of acetic acid, both alone and in the presence of the poisons indicated, the catalyst consisting of 0·005 gram of platinum. The linear character of this curve is further exemplified by the various results detailed in connexion with the work about to be described.

The measurements of the rate of absorption of hydrogen were, in every case, carried out at 50° in the apparatus previously employed for lead. It will be seen that, both with and without poisons, the point of inflexion occurs in a region immediately preceding saturation.

Action of Mercury.

The solution employed for poisoning was made by dissolving 0·108 gram of pure mercuric oxide in 100 c.c. of glacial acetic acid. Each c.c. thus corresponded with 1 mg. of mercury.

On adding varied amounts of this solution to a reaction mixture, consisting of 3 c.c. of oleic acid, 0·005 gram of platinum, and sufficient glacial acetic acid to amount, with that added with the poison, to 9 c.c. of the solvent, the following results were obtained. The temperature, both for this series and for all measurements recorded in the present paper, was 50°.

The absorption curves are in each case approximately linear, and the activity can consequently be read off directly without differentiation. As before, the relative activity of the platinum, in the presence of the given concentration of inhibitant, has been taken as being proportional to the number of c.c. of hydrogen absorbed per minute. In cases where the reaction curve obtained

TABLE I.

C.c. of Hg solution added.	Hydrogen absorption in c.c. after				
	1 min.	2 mins.	3 mins.	4 mins.	5 mins.	10 mins.
0·0	21·0	43·5	67·0	90·0	113·0	185·0
0·25	16·0	32·5	49·1	65·6	81·6	156·4
0·5	10·8	21·8	33·0	43·6	54·6	104·6
0·75	5·6	11·8	17·5	23·0	28·4	51·2
0·95	2·8	5·2	7·6	10·2	12·6	24·8
1·25	2·2	4·0	6·0	8·0	9·8	—
1·5	1·3	2·8	4·3	5·8	7·2	13·9
2·0	1·0	1·8	2·6	3·3	3·8	—
3·0	0·1	0·3	0·4	0·6	0·8	1·8

has been found to deviate subsequently from the ideal linear form, the rate of absorption of hydrogen during the first few minutes has been taken as being representative of the activity of the platinum.

The variation of catalytic activity with the mercury content of the system is given in table II.

TABLE II.

Mercury content of system in milligrams.	*Ratio gram-*atom Hg to gram-atom Pt.	*Catalytic activity of* platinum in terms of c.c. H_2 fixed per min.
0·0	0·0	22·5
0·25	0·049	16·5
0·5	0·097	11·0
0·75	0·146	5·7
0·95	0·185	2·6 (point of inflexion)
1·25	0·244	2·0
1·5	0·292	1·4
2 0	0·390	0·9
3 0	0·585	0·15

If the above results are plotted graphically, the inhibitive effect is seen to be a linear function of the mercury present in the reacting system almost down to complete extinction of activity, in which region a point of inflexion occurs. The residual catalytic activity then decreases less rapidly with increasing mercury content than is required by the linear law. With sulphur, this point of inflexion would appear to be somewhat lower than with mercury, whilst arsenic and zinc deviate from the linear course at a slightly higher point.

In the case of lead, under the conditions previously employed, the presence of a similar point of inflexion in the neighbourhood of total suppression of activity was not noted, but it is possible that the existence of a small residual activity was masked by

"clogging" poisons, by the action of which catalytic activity of a relatively low magnitude would be quickly suppressed.

Action of Sulphur.

The poison was here employed in the elementary form dissolved in glacial acetic acid, in which solvent sulphur is slightly, but sufficiently, soluble. Each c.c. of the solution contained 0·069 mg. of sulphur.

The progress of the absorption of hydrogen by a reacting system of the usual nature, in the presence of various concentrations of the inhibitant, is summarised in table III.

TABLE III.

C.c. of sulphur solution added.	Hydrogen absorption in c.c. after					
	1 min.	2 mins.	3 mins.	4 mins.	5 mins.	10 mins.
0·0	21·0	43·5	67·0	90·0	113·0	185·0
0·2	20·0	39·5	60·0	80·5	100·5	182·0
0·4	18·2	36·2	53·8	70·0	86·0	162·0
0·8	15·0	29·2	42·5	55·0	66·5	118·5
1·2	10·8	21·8	32·6	42·6	52·1	93·1
1·6	5·5	11·8	18·1	24·1	29·8	52·5
2·0	1·6	3·0	4·6	6·1	7·4	13·7
2·2	1·0	2·1	3·1	4·4	5·5	10·8
2·7	0·5	0·9	1·2	1·5	1·7	3·2
2·9	0·5	1·0	1·5	1·9	—	—
3·5	0·2	0·4	0·6	0·7	0·9	—

The variation of catalytic activity with the concentration of the inhibitant is given in table IV.

TABLE IV.

Sulphur content of system in *milligrams.*	Ratio gram-atom S to *gram-atom* Pt.	Catalytic activity *of platinum.*
0·0	0·0	22·5
0·014	0·017	20·0
0·028	0·034	18·0
0·055	0·067	15·0
0·083	0·101	10·8
0·110	0·134	6·0
0·138	0·168	1·5 (point of inflexion)
0·154	0·188	1·1
0·186	0·228	0·5
0·20	0·244	0·5
0·24	0·292	0·2

The above results, when plotted graphically, form a curve similar to that obtained for mercury.

Action of Arsenic.

The inhibitive solution was made by dissolving 6·6 milligrams of arsenious oxide in a small quantity of distilled water and diluting to 50 c.c. with acetic acid. Each c.c. thus contained 0·1 mg. of arsenic.

A series of measurements of the rate of absorption of hydrogen by 3 c.c. of oleic acid in the presence of 0·005 gram of platinum and various known concentrations of arsenic is summarised in table V, the experiments being carried out under the usual conditions.

TABLE V.

C.c. of arsenic solution added.	Hydrogen absorption in c.c. after					
	1 min.	2 mins.	3 mins.	4 mins.	5 mins.	10 mins.
0·0	20·0	40·1	59·8	79·0	96·4	181·0
0·25	17·2	35·0	52·3	69·8	86·0	170·5
0·5	12·5	26·0	39·7	53·6	67·5	134·2
0·75	11·5	23·0	34·5	45·5	56·5	107·0
1·0	9·0	18·0	27·5	37·0	46·0	88·7
1·25	6·6	13·0	19·0	24·7	30·0	48·0
1·5	4·9	10·0	14·9	19·5	23·8	39·6
2·25	2·0	4·0	5·8	7·9	9·7	—
2·5	1·3	2·0	3·4	4·2	4·9	—
3·0	0·6	1·1	1·6	1·9	2·2	—
3·5	0·3	0·5	0·7	0·8	1·0	—

The variation in catalytic activity of the platinum with increasing arsenic content is given in table VI, the poisoning curve being of the usual linear type.

TABLE VI.

Arsenic content of system in milligrams.	Ratio gram-atom As to gram-atom Pt.	Catalytic activity of platinum.
0·0	0·0	20·0
0·025	0·013	17·5
0·05	0·026	13·7
0·075	0·039	11·5
0·10	0·052	9·2
0·125	0·065	6·6
0·15	0·078	4·9 (point of inflexion)
0·225	0·117	2·0
0·25	0·13	1·1
0·30	0·156	0·5
0·35	0·182	0·3

Action of Zinc.

The zinc solution was made by dissolving 8·3 milligrams of pure zinc oxide in 100 c.c of glacial acetic acid. Each c.c. thus corre-

sponded with 0·067 mg. of zinc. The absorption of hydrogen by 3 c.c. of oleic acid under the usual conditions is summarised in table VII.

TABLE VII.

C.c. of zinc solution added.	Hydrogen absorption in c.c. after					
	1 min.	2 mins.	3 mins.	4 mins.	5 mins.	10 mins.
0·0	20·0	40·1	59·8	79·0	96·4	181·0
0·5	14·4	28·5	41·7	53·7	65·4	125·7
1·0	9·8	18·8	28·0	37·2	46·2	90·4
1·5	4·7	9·2	13·7	18·2	22·5	41·7
1·8	3·6	7·0	10·3	13·5	16·6	—
3·0	0·5	0·9	1·3	1·7	2·1	—
4·0	0·0	0·2	0·3	0·4	0·4	—

The variation in the activity of the platinum catalyst with the various concentrations of zinc is summarised in table VIII. The poisoning curve is of the usual linear form, the point of inflexion being, however, somewhat higher both for zinc and arsenic than for mercury and sulphur.

TABLE VIII.

Zinc content of system in milligrams	Ratio gram-atom Zn to gram-atom Pt.	Catalytic activity of platinum.
0·0	0·0	20·0
0·034	0·02	14·3
0·067	0·04	9·2
0·10	0·06	4·5 (point of inflexion)
0·12	0·071	3·6
0·20	0·12	0·4
0·27	0·16	0·1

It has previously been mentioned that, in order to avoid the complication which would be introduced by the possible coagulation of a colloid in the presence of an electrolyte, non-colloidal in place of colloidal platinum was employed for the present measurements. In view, however, of the rather indefinite line of demarcation between colloidal and finely divided, non-colloidal particles, such as are formed by the reduction of carefully ground, metallic oxides in an oil suspension, it was considered interesting to investigate, in addition, the influence of an acetate containing a metallic ion, which, from its nature, would not be expected to be poisonous. It may perhaps be stated, however, that in no case did visible flocculation occur during any of the measurements described in the present paper, although this frequently occurring phenomenon has been noticed in another series carried out at a higher temperature.

The indifference of the catalytic activity of platinum to the presence of a metallic acetate of this nature, even in concentration somewhat in excess of those employed for the poisoning experiments, is illustrated by the following measurements of the relative rates of absorption of hydrogen by 3 c.c. of oleic acid and 0·005 gram of platinum, with and without the addition of potassium acetate. The experiments were carried out at 50° under the usual conditions. The potassium acetate solution was made by dissolving 50 milligrams of the salt in 100 c.c. of acetic acid, 1 c.c. of this solution being added to the reacting system. Reference to table IX shows that no inhibition of activity occurred.

TABLE IX.

Time in minutes.	Hydrogen absorption in c.c.	
	System without potassium acetate.	System with potassium acetate.
1	23·6	24·0
2	48·0	49·0
3	72·0	75·0
4	96·3	100·4
5	121·0	127·0
6	146·0	153·0
7	168·0	178·0

It is a matter of experience that catalysts of relatively high activity are more susceptible to poisoning than those of lower activity, and, for this reason, work is being carried out on the influence of variations in the surface of the catalyst on the slope of the various poisoning curves.

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WALSALL.
[*Received, January 15th, 1921.*]

XXVIII.—*On Reduction by Metals in Acid Solutions. Part I. The Reduction of Acid Ferric Sulphate Solutions by Zinc and Magnesium.*

By SAMUEL SUGDEN.

THE reduction of ferric sulphate solutions containing free sulphuric acid by zinc, magnesium, and iron was studied by Thorpe (T., 1882, **41**, 287), who found that the amount of reduction brought about by the metal increased as the ferric sulphate concentration increased, and decreased with increasing concentrations of free

acid. The solutions examined were moderately dilute, and only covered a small range of concentrations.

In the present paper, similar experiments are described covering nearly the whole available range of concentrations. These reveal a marked difference between the behaviour of zinc and magnesium.

Experimental.

Materials.—Zinc foil, 0·0107 cm. thick, cut into pieces 0·19 cm. by 0·72 cm., was used; 0·3268 gram was weighed out for each experiment. The initial surface area of this amount of the metal was calculated to be 9·3 sq. cm.* The foil contained 99·7 per cent. of zinc, weighed as oxide. A trace of lead was present, but no other metallic impurities were detected.

The magnesium was in the form of ribbon 0·0158 cm. thick. This was cut into pieces 0·27 cm. by 0·70 cm.,† and 0·1216 gram used in each experiment. The initial surface area was calculated to be 9·5 sq. cm. The ribbon contained 98·7 per cent. of magnesium, weighed as pyrophosphate. A minute amount of silica was found on examination of a solution of the metal in nitric acid, but no metallic impurities.

Considerable difficulty was experienced in purifying the ferric sulphate in large amounts. The method finally adopted was as follows. Concentrated sulphuric acid was added to a filtered, hot solution of 1 kilo. of the commercial salt in 1 litre of water until a faint turbidity was produced. After keeping for several hours. the viscous mother liquor was filtered from the granular crystals of the acid sulphate, which were washed with alcohol and dried in air. About 6 kilo. of the hydrated acid sulphate were prepared in this manner.

A stock solution was prepared by dissolving the acid sulphate in water and adding the requisite amount of ferric hydroxide. This solution, corresponding in composition with the neutral or slightly basic salt, was analysed, and the experimental solutions prepared from it.

The sulphuric acid used in making the solutions was free from chlorides and nitrates, and contained only minute traces of arsenic.

Experimental Conditions.—Fifty c.c. of the solution were placed in a small flask, the weighed amount of the metal added, and the flask shaken frequently until the metal had all dissolved. The

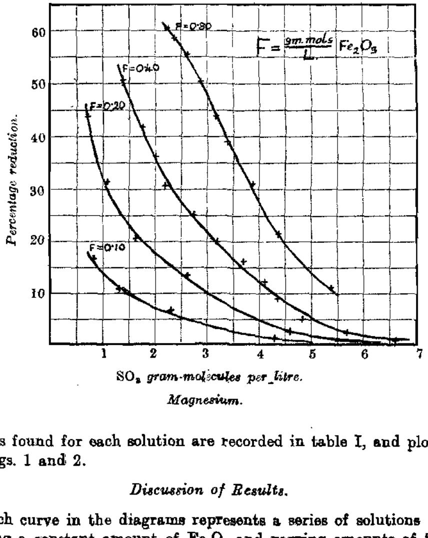
* Average value for 200 pieces chosen at random. The surface area is determined chiefly by the thickness, and is not appreciably altered by small variations in the length and breadth. Small pieces were used to facilitate stirring.

† Average value for 200 pieces chosen at random.

time required for complete solution was noted, and the ferrous salt formed estimated by titration with $N/10$-permanganate solution.

All the experiments were carried out in duplicate at the ordinary temperature (18—21°). With most of the solutions, the results were found to be very consistent, the difference between the values found in duplicate experiments being less than 1 per cent. In some of the experiments with zinc, which lasted for several hours (solutions 5, 6, 8), somewhat larger differences were found, and a small amount of oxidation by air may have occurred. The mean

FIG. 1.



Magnesium.

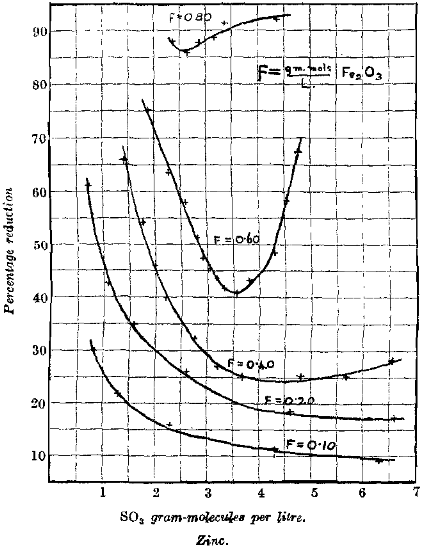
values found for each solution are recorded in table I, and plotted in Figs. 1 and 2.

Discussion of Results.

Each curve in the diagrams represents a series of solutions containing a constant amount of Fe_2O_3 and varying amounts of SO_2. The ordinates represent the amount of reduction observed, expressed as a percentage of that theoretically possible if no hydrogen were evolved. To save space, this number is referred to in the table and in the text as the "percentage reduction," as the use of

this term does not imply any hypothesis regarding the mechanism of the reaction. The left-hand end of each curve therefore represents a neutral or a feebly acid solution, in which the metal dissolves slowly. The curves were extended to the right, the limits corresponding with solutions from which crystals of the acid sulphate were deposited, or, for the more dilute solutions, in which

FIG. 2.



a concentration of 6 gram-molecules of free acid per litre was reached.

With both zinc and magnesium, the addition of acid to a nearly neutral solution produces a decrease in the percentage reduction. With magnesium, this continues throughout the whole range of concentrations, but with zinc a minimum is reached, and then the

percentage reduction increases rapidly. A new type of reaction appears to set in; the zinc becomes dull grey in colour, and dissolves much more slowly, with a scarcely perceptible evolution of gas. This peculiar behaviour of zinc is most marked with the solutions containing higher concentrations of ferric oxide, but even the most dilute solutions give curves which differ in shape from the corresponding curves for magnesium. The gradual replacement of the rapid reaction by the slow one is well seen in solutions 21 and 22. The zinc dissolves rapidly at first, changes in appearance after a few minutes, and then dissolves slowly, with very little evolution of gas.

In this connexion, it should be mentioned that Pring and Tainton (T., 1914, **105**, 710), in studying the electro-deposition of zinc from solutions of zinc sulphate containing about 1 gram-molecule of free sulphuric acid per litre, found that the ratio of zinc to hydrogen liberated at the cathode increased with increasing concentrations of acid.

The time required for solution gives an approximate estimate of the relative rates of reaction of the metals in the different solutions. Remarkable variations in this rate were observed. Thus the zinc, which dissolved in an hour in a solution containing 0·80 gram-molecule of ferric oxide per litre, and rather less acid than was required for the neutral salt, was not completely dissolved in twenty-four hours in a solution containing the same amount of ferric oxide and 2 gram-molecules of free acid per litre. This behaviour cannot be ascribed to the presence of so much free acid, because solutions containing much more acid, but less ferric salt, dissolve the same amount of zinc in a few minutes.

With magnesium, the time required for solution falls off continuously as the concentration of free acid increases, and finally reaches a limiting value of just less than a minute with all concentrations of ferric salt.

It is difficult to reconcile these results with the theory that nascent hydrogen owes its activity to the presence of free atoms, as, on this view, the activity should decrease continuously with increasing acidity for both metals. The theory of direct reduction by the metal is also inadequate, for even if the assumption is made that zinc can directly attack the ferric sulphate in weakly acid solutions at a speed comparable with its rate of solution in the acid, the existence of a perturbing condition has to be recognised in the case of zinc in the more concentrated solutions, which not only modifies the relative velocities of the two reactions, but also lowers markedly the velocity of solution.

It is hoped to extend these experiments to other metals and

oxidising agents, and to investigate the effect of varying the temperature and pressure.

TABLE I.

Soln.	Fe_2O_3 gram-mols. per litre.	SO_3 gram-mols. per litre.	Magnesium. Time, mins.	Magnesium. Percentage reduction.	Zinc. Time, mins.	Zinc. Percentage reduction.
1	0·80	2·25	15	60·6	—	—
2	,,	2·40	6	58·5	60	88·1
3	,,	2·65	2·5	55·6	90	85·9
4	,,	2·90	2	50·6	400	87·9
5	,,	3·15	,,	44·0	ca. 1000	88·7
6	,,	3·40	1·5	39·0	ca. 2000	91·6
7	,,	3·90	,,	31·2	—	—
8	,,	4·40	,,	21·8	ca. 2000	92·3
9	,,	5·40	1	11·4	—	—
10	0·60	1·93	—	—	13	75·2
11	,,	2·30	—	—	6	63·8
12	,,	2·60	—	—	6	57·9
13	,,	2·80	—	—	4	51·3
14	,,	2·93	—	—	3	47·3
15	,,	3·05	—	—	,,	45·6
16	,,	3·18	—	—	,,	43·8
17	,,	3·30	—	—	,,	42·1
18	,,	3·55	—	—	,,	41·1
19	,,	3·80	—	—	,,	43·4
20	,,	4·30	—	—	,,	48·5
21	,,	4·55	—	—	200	58·5
22	,,	4·80	—	—	,,	67·5
23	0·40	1·43	8	50·7	30	66·1
24	,,	1·73	1·5	42·0	6	54·3
25	,,	1·98	1	36·5	5	46·2
26	,,	2·20	,,	31·0	3·5	40·0
27	,,	2·73	,,	25·3	3	32·7
28	,,	3·20	,,	20·0	2·5	27·2
29	,,	3·70	,,	16·6	,,	25·2
30	,,	4·12	,,	12·4	—	—
31	,,	4·34	,,	9·0	—	—
32	,,	4·78	,,	4·9	2	25·6
33	,,	5·66	,,	2·1	3	25·6
34	,,	6·55	,,	0·4	60	28·4
35	0·20	0·72	30	44·0	60	61·5
36	,,	1·10	4	30·7	32	42·7
37	,,	1·60	1·5	20·7	27	35·0
38	,,	2·60	1	13·2	14	26·0
39	,,	4·60	,,	2·5	9	18·3
40	,,	6·60	,,	1·5	20	17·6
41	0·10	0·80	2	17·0	60	30·0
42	,,	1·30	1	11·1	40	22·0
43	,,	2·30	,,	6·9	32	15·9
44	,,	4·30	,,	1·5	16	11·4
45	,,	6·30	,,	0·8	11	9·2

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[*Received, January 17th, 1921.*]

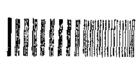
XXIX.—*Phenomena of the Ignition of Gaseous Mixtures by Induction Coil Sparks.*

By JOHN DAVID MORGAN and RICHARD VERNON WHEELER.

HIGH-TENSION sparks produced at a gap in the secondary circuit of an induction coil when a current in the primary circuit is broken are, in general, of a complex character. For the purposes of the present paper, it is sufficient to direct attention to two main characteristics which are apparent when the sparks are viewed in a revolving mirror or photographed on a moving plate or film.

With a current in the primary circuit in considerable excess of that just necessary to produce a spark at a gap in the secondary circuit, the image of the spark is found to comprise (*a*) an intensely luminous initial line, and (*b*) a slightly luminous band. This band is usually striated, the striations being due to oscillations in the electric discharge. These characteristics are reproduced diagrammatically in Fig. 1.

FIG. 1.



The first part, *a*, of the spark, which has been termed the "capacity component," resembles the spark obtained by a single discharge from a Leyden jar, whilst the second part, *b*, termed the "inductance component," resembles (save for the striations) the break-flash obtained when a current in an inductive circuit is interrupted by the separation of metallic contacts. The striations in the band, *b*, are most marked near its beginning, and they gradually fade away into a region of uniform colour towards the end of the spark.

This description of the characteristics of high-tension sparks refers to those produced when the current broken in the primary circuit is in considerable excess of that just necessary to produce any spark at all at the gap in the secondary circuit. When the primary current is reduced to an amount approaching the minimum at which a spark can be obtained, there is a modification in the character of the spark, particularly when a large coil (a "10-inch" coil, for example) is used to produce a short spark (1 or 2 mm. in length). A photograph of such a spark on a rapidly revolving film discloses more than one intensely bright line, each followed by a luminous band. At the limit, when the primary current is only just sufficient to produce a spark at the gap in the secondary circuit, the luminous bands almost disappear, and the spark appears to consist of a single bright line.

The total heat energy, *J*, of the induction-coil spark is derived from the electromagnetic energy associated with the primary circuit

of the coil at the instant of interruption of the current. The proportion of this energy that appears as heat in the spark depends on a number of factors. For a given width and character of gap, it may be represented by the expression $J = cLi^2$, in which L is the inductance of the primary circuit, i is the current flowing in that circuit at the moment of break, and c is a factor the value of which (always less than 0·5) depends on the coil and its accessories and the nature of the spark-gap. The total energy is distributed between the capacity and inductance components of the spark.

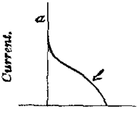
The energy of the capacity component alone, J_1, is expressed with sufficient accuracy, so long as the component consists (as is usual) of a single discharge, by the formula $J_1 = \frac{1}{2}CV^2$, in which C is the capacity associated with the gap circuit (including that of the secondary winding) and V is the voltage at which the spark is initiated. The value of C can be varied by varying the arrangement of the apparatus, but is independent of the magnitude of the current in the primary circuit. The value of V depends on the shape and disposition of the sparking electrodes and on the nature and condition of the gases between them. With some spark-gaps, particularly with those formed between sharp points, the value of V also depends on the rate of application of voltage, which, with a given induction coil and interrupter, depends on (1) the capacities of the primary and secondary circuits, (2) the primary current at the moment of break, and (3) insulation leakage in the secondary circuit. (For a discussion of the effects of leakage, see Bairsto, *Inst. Elect. Eng.*, 1920, **58**, 507.) Keeping other conditions constant, the manner in which V (the sparking voltage) varies with i (the primary current at break) differs with the gap. In some gaps (for example, ball gaps) the variation is small, whilst in others (for example, point gaps) it is relatively large. When the voltage is applied suddenly and for a very short interval of time, as when an induction coil is used, the sparking voltage is higher than when the voltage is applied slowly. The ratio between the impulsive sparking voltage (peak value) and the static or slowly applied sparking voltage is termed the "impulse" ratio (see Peek, "Dielectric Phenomena in High Voltage Engineering," New York, 1915).

The energy of the inductance component alone, J_2, can be represented by the difference between the quantities cLi^2 and $\frac{1}{2}CV^2$. With a given coil and a given setting of the spark-gap, the energy of the inductance component depends mainly on the value of i, though it also depends on V, since that quantity is affected by the value of i. It is important to note, also, that the energy of the inductance component is affected by the working conditions

of the interrupter in the primary circuit and by insulation leakage in the secondary circuit.

The *duration* of the capacity component is extremely short, and depends only on conditions in the gap circuit; that of the inductance component is relatively long, and (the condition of the secondary circuit remaining constant) is dependent on the value of *i*. Oscillograph records of the duration and magnitude of the current in an induction-coil spark are usually of the type shown in Fig. 2. The line *a* (which cannot be resolved by the oscillograph) represents the current in the capacity component, and the curve *b* that in the inductance component.

FIG. 2.



The fact that high-tension sparks obtained from induction coils are of a complex character raises the question of the manner in which the ignition of gaseous mixtures is effected by them. Evidence has been advanced in support of the suggestion that in certain instances ignition is due solely to the capacity component of the spark (Paterson and Campbell, *Proc. Physical Soc.*, 1919, **31**, 193; Morgan, "Principles of Electric Spark Ignition," London, 1920).

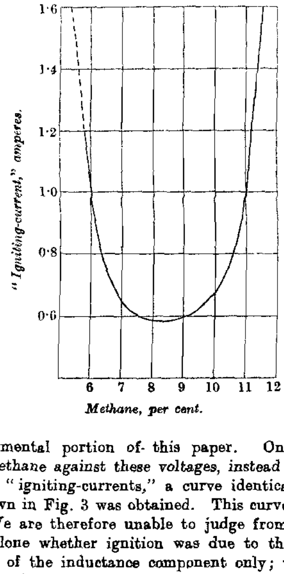
This hypothesis was adopted when discussing the ignition of mixtures of methane and air by the impulsive electrical discharge (T., 1920, **117**, 903), though it was not assumed that the hypothesis had been definitely proved. In the present paper, the question is considered anew in the light of further experiments on the ignition of mixtures of methane and air under different conditions.

In the first series of experiments, a number of different mixtures of methane and air were employed, and determinations were made of the minimum currents ("igniting-currents") which, when broken in the primary circuit of an induction coil, would produce sparks at a gap of constant width in the secondary circuit capable of igniting the mixtures. The spark-gap was formed between a pair of sharply pointed platinum wires, and was about 1 mm. in width. The precautions taken in carrying out the experiments to ensure accuracy of the results have been described in T., 1920, **117**, 903. The results are shown in Fig. 3.

It will be seen that the curve is a smooth one, and that there is a gradual increase in the "igniting-current" as the percentage of methane in the mixture is decreased or increased on either side of the range 8·2—8·4. When the width of the spark-gap is

constant, the "igniting-current" (that is to say, the current broken in the primary circuit) is a measure of the total energy of the spark, for $J = cLi^2$, so that the relationship shown in Fig. 3 is consistent with the supposition that ignition of the mixtures was dependent on the total energy of the sparks. Ignition might equally as well be dependent only on the energy of the capacity component, however, which depends essentially on the sparking voltage ($J_1 = \frac{1}{2}CV^2$). Determinations were therefore made of the voltages (peak-values) of the sparks produced at a number of the "igniting-currents" recorded in Fig. 3, in the manner described

FIG. 3.

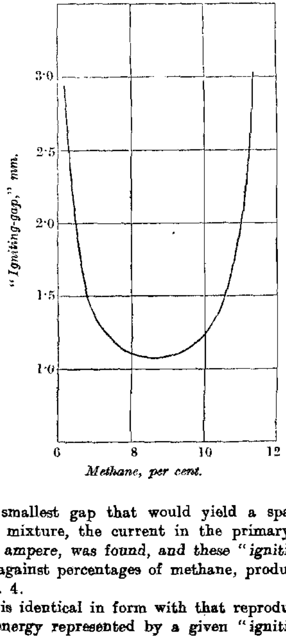


in the experimental portion of this paper. On plotting percentages of methane against these voltages, instead of against the corresponding "igniting-currents," a curve identical in character with that shown in Fig. 3 was obtained. This curve is reproduced in Fig. 6. We are therefore unable to judge from this series of experiments alone whether ignition was due to the total energy or the energy of the inductance component only; the results are consistent with either theory.

In a second series of experiments, with a number of mixtures of methane and air, a current of constant value (1 ampere) was

broken in the primary circuit of the induction coil, and the energy of the spark at the spark-gap was varied by varying the width of that gap. The gaps were formed between a disk of platinum and a fine point of platinum to which a micrometer was attached, enabling the widths of the gaps to be read accurately to one-hundredth of a millimetre. The explosion-apparatus employed is shown diagrammatically in Fig. 8; the precautions observed in carrying out the determinations were as in the first series of experi-

FIG. 4.



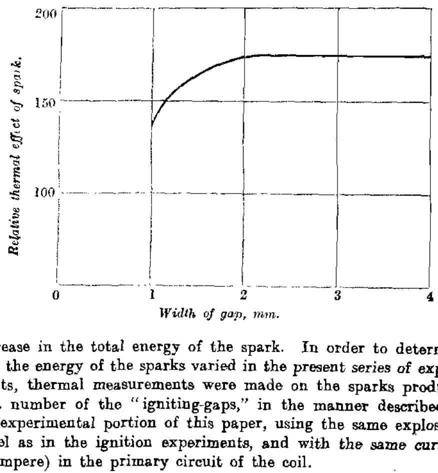
ments. The smallest gap that would yield a spark capable of igniting each mixture, the current in the primary circuit being constant at 1 ampere, was found, and these "igniting-gaps" were then plotted against percentages of methane, producing the curve shown in Fig. 4.

This curve is identical in form with that reproduced in Fig. 3, so that the energy represented by a given "igniting-gap" bears the same relationship to the mixture ignited as does the energy

corresponding with the "igniting-current" for that mixture. This being so, knowledge of the manner in which the energy of the induction-coil spark as a whole, and the energy of its capacity component, vary with the width of the gap at which the spark passes, should determine the question whether the capacity component alone is effective in causing ignition.

When the primary current is maintained constant, as in this series of experiments, the total energy of the spark of an induction coil usually increases with increase of width of gap until a maximum is reached, after which it may remain constant over a considerable range of width of gap; eventually, a stage is reached at which an increase in the width of the gap is accompanied by a

FIG. 5.



decrease in the total energy of the spark. In order to determine how the energy of the sparks varied in the present series of experiments, thermal measurements were made on the sparks produced at a number of the "igniting-gaps," in the manner described in the experimental portion of this paper, using the same explosion-vessel as in the ignition experiments, and with the same current (1 ampere) in the primary circuit of the coil.

The results are shown in Fig. 5, in which the deflections of a galvanometer, corresponding with the thermal effects of the sparks, are plotted against the widths of gap at which those sparks were produced. The galvanometer deflections give relative values for the total energies of the sparks. It will be seen that the energy of the sparks increased gradually as the width of the gap was

increased up to 2 mm., and then remained constant up to 4 mm. For the interpretation of the ignition experiments (Fig. 4), the results for gaps between 1 and 3 mm. in width only need be considered. On plotting values obtained from Fig. 5 instead of gap-widths, the relationship between percentages of methane in the mixture and the total energy of the sparks that ignited them is found to be very different from the relationships shown in Figs. 3 and 4. It follows, in fact, from these thermal measurements that, if the total energy of the spark is required for ignition, the same energy is required to ignite all mixtures of methane and air containing less than 6·5 or more than 11 per cent. of methane, which is contrary to fact.

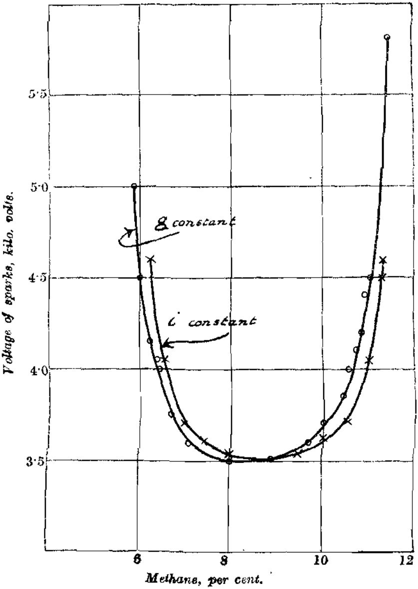
On the other hand, measurements of the voltages (V) of the sparks produced at given "igniting-gaps" (made under the same conditions as the ignition experiments) gave results which, when plotted against the corresponding percentages of methane, produced a curve (Fig. 6) in close agreement with those shown in Figs. 3 and 4. This second series of experiments, therefore, definitely ascribes the igniting-power of the induction-coil sparks to the energy of their capacity components ($J_1 = \frac{1}{2}CV^2$), and not to their total energy.

It has been assumed during the discussion of these results (1) that so long as the experimental conditions under which the sparks are produced are constant (that is to say, so long as the general character of the sparks is unchanged), the energy required to ignite a given mixture is constant, and (2) that ignition is essentially a thermal process involving the heating of a sufficient volume of the inflammable mixture at a sufficient temperature during a sufficient length of time.

The first assumption needs no argument to support it, but the corollary, that the least energy required to ignite a given mixture may vary with the character of the spark, requires, perhaps, amplification. When describing the general characteristics of induction-coil sparks, enough has been said to show that the distribution of energy between the capacity and inductance components of a spark can be varied by altering the experimental conditions. For example, the energy of the capacity component can be varied by varying either C, the capacity associated with the gap circuit, or V, the voltage at which the spark is initiated. The latter, as already stated, is mainly dependent on the shape and arrangement of the electrodes and the rate of application of the voltage. Under certain conditions, it is possible so to reduce the proportion of the total energy of an induction-coil spark that appears in its capacity component as to render that component

incapable of igniting a given mixture. It does not necessarily follow, however, that a spark capable of igniting the mixture cannot then be produced; on the contrary, if there is sufficient energy in the inductance component, ignition will occur. The energy required for the ignition of a mixture by an "inductance"

FIG. 6.

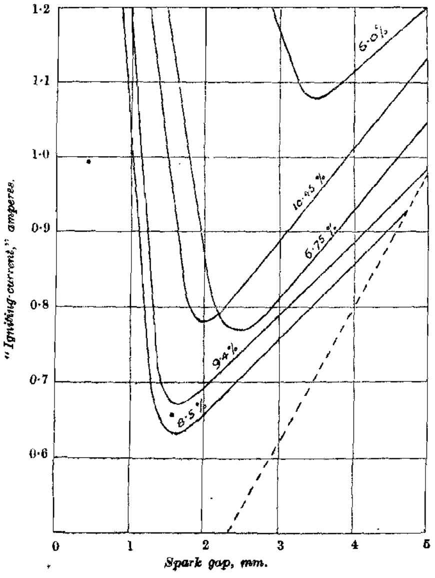


spark is, however, considerably greater than that required for ignition of the same mixture by a "capacity" spark. When the complex sparks produced by induction coils are used and the capacity component is of itself insufficient to cause ignition, the ignition due to the supplementary action of the inductance component is capricious.

In general, the energy required for the ignition of a given

mixture by a pure capacity spark can be varied by altering either the sparking voltage or the capacity of the spark circuit, and the energy required for ignition by a pure inductance spark can be varied by altering the impressed (or circuit) voltage. Hence the necessity, when attempting to explain the chemical and physical phenomena of the ignition of gaseous mixtures by electrical means,

FIG. 7.



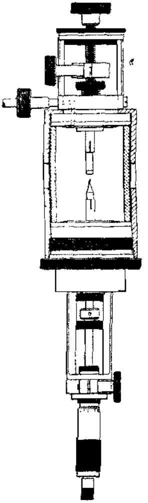
of maintaining constancy in the characteristics of the electric sparks, lest change in the sparks be mistaken for change in the mode of ignition of the mixture.

The second assumption—a thermal process of ignition—implies, as is generally recognised, that the energy of an electric spark is not the only factor to be considered, but that the mode of application of that energy, its duration, and its concentration (and any

concomitant phenomena, such as the production of a pressure wave between the electrodes) must be taken into account. In the experiments under review, ignition was by the capacity component of an induction-coil spark. The duration of this component has been shown (p. 241) to be exceedingly short, so short that it is highly improbable that any effective alteration could be made in it by changes in the experimental conditions. The concentration of the capacity component might, however, be susceptible of considerable change by change in the width of the spark-gap. With a view to explore further the rationale of ignition of gaseous mixtures by electric sparks, a relationship was therefore sought between the "igniting-current" and the spark-gap for any given mixture of methane and air.

Typical examples of the relationship found are shown diagrammatically in Fig. 7, in which, for several mixtures of methane and air, the "igniting-currents" corresponding with different lengths of spark-gap are recorded. The dotted line in the diagram records the least current in the primary circuit of the induction coil, which, when broken, would produce any spark at all at the gap in the secondary circuit. It will be seen that this line cuts the curve for the 8·5 per cent. mixture when the gap is 4·7 mm. wide, so that the true "igniting-current" with wider gaps cannot be determined, the first spark that passes causing ignition of the mixture. These experiments were made in the same apparatus (Fig. 8) as was used for the series recorded in Fig. 4.

FIG. 8.



With any mixture of methane and air, it was found that the "igniting-current" at first rapidly decreased as the spark-gap was widened, but that there was a well-defined optimum width, after passing which each further increase resulted in a regular increase in the "igniting-current." The value of the width of spark-gap that enabled ignition to be effected most readily (in the sense that it required the lowest current in the primary circuit of the coil to be broken to produce a secondary discharge of sufficient energy) depended on the composition of the mixture. Thus, for the mixtures

of methane and air tested, the optimum spark-gaps, and the "igniting-currents" with those gaps, were:

Methane, per cent.	Optimum spark-gap. Mm.	"Igniting-current" with optimum spark-gap. Amperes.
6·00	3·5	1·08
6·75	2·5	0·77
7·40	2·0	0·67
8·05	1·7	0·64
8·50	1·6	0·63
8·70	1·6	0·63
8·95	1·6	0·64
9·40	1·7	0·67
10·50	2·0	0·78
11·40	3·0	0·92
12·40	4·5	1·52

If the optimum spark-gaps are plotted against percentages of methane, a curve of the same characteristics as those reproduced in Figs. 3 and 4 is obtained. This relationship is dependent on a physical property of the mixtures (their ability to propagate flame), and need not be discussed in this paper, which deals with the characteristics of the sparks.*

We have seen that, so long as the general electrical characteristics of the sparks are not altered, there should be no change in the energy of a spark required to ignite a given mixture, except in so far as it may be possible to effect a change in the mode of application of that energy. Measurements were made of the voltages (representing the energies of the capacity components) of the sparks obtained with gaps and currents corresponding with points on such curves as those reproduced in Fig. 7, and it was found that the voltage of a spark that ignited a given mixture remained constant over the whole of the left-hand limbs of the curves, and showed but a slight increase for a little way up the right-hand limbs. For example, with the mixture containing 6·75 per cent. of methane, the voltage of the capacity component of the spark that effected ignition was the same when the spark-gap was 1·5 mm. in width and a current of 1·2 amperes was broken in the primary circuit of the coil as when the current broken was 0·85 ampere and the width of the gap was 2 mm.

The greater part of the ascending limb of each curve, however,

* An explanation can now be given of the statement made in a previous paper that the graph reproduced in Fig. 4 is complete, the terminal points of the curve representing "limits" of igniting power of the sparks. With a constant current of 1·0 ampere in the primary circuit of the coil, mixtures containing less than about 6·0 or more than about 11·5 per cent of methane cannot be ignited by the secondary discharge under the conditions of the experiments, whatever the width of the gap, as is shown by the curves in Fig. 7.

represents a definite and regular increase in the sparking voltage. In other words, as the spark became more attenuated, its energy-content had to be greater to enable it to ignite a given mixture. Within certain limits, dependent on the composition of the mixture, the dimensions of a spark (the concentration of its energy) have an inappreciable effect on its igniting-power, but, as was anticipated, on the assumption that the ignition of gaseous mixtures by electric sparks is a thermal phenomenon, a decrease in the *concentration of the energy eventually requires that a greater* quantity shall be supplied.

EXPERIMENTAL.

Ignition Experiments.—Details of the explosion vessel used for the first series of determinations, and of the method of conducting

FIG. 9.

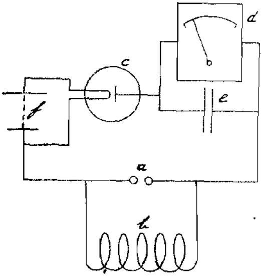
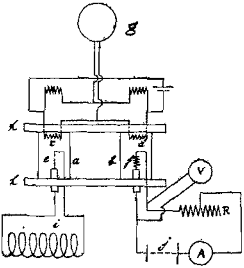


FIG. 10.



the experiments, have been given in previous communications. A diagram of the explosion vessel used for the second and third series of experiments is shown in Fig. 8, and requires no description.

Voltage Measurements.—The apparatus used is shown diagrammatically in Fig. 9. A thermionic valve, *c*, electrostatic voltmeter, *d*, and small condenser, *e*, are arranged in conjunction with the spark-gap, *a*, which is in the secondary circuit of the induction coil, *b*, the filament of the valve being heated by current from an insulated battery, *f*, to which the negative end of the induction coil is connected. (For a discussion of certain precautions to be

observed when using this apparatus, see Campbell and Patterson, *Phil. Mag.*, 1919, **37**, 480.)

Thermal Measurements.—A pair of glass chambers, *a*, *b* (Fig. 10), carried between ebonite plates, *h*, contain, respectively, the spark-gap, *e*, and a heating coil, *f*. Each chamber is fitted with a resistance, *c*, *d*, of fine platinum wire, forming part of a Wheatstone bridge. The spark-gap, *e*, is connected with the secondary circuit, *i*, of an induction coil, and the heating coil, *f*, is connected with the circuit of a battery, *j*, containing an ammeter, *A*, a voltmeter, *V*, and a variable resistance, *R*. Starting with the galvanometer of the Wheatstone bridge, *g*, at zero, the heating effect due to sparks passing in quick succession in *a* causes a variation in the resistance of *c*, and a corresponding deflection of the galvanometer. The needle of the galvanometer can be brought back to zero on producing an equal heating effect in *b* by causing a measured current to flow in the heating coil, *f*. Knowing the watts consumed by the heating coil, and the number of sparks passing per second in *a*, the energy per spark, in joules, can be calculated.

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[*Received, January 4th*, 1921.]

XXX.—*The Action of the Grignard Reagent on certain Nitric Esters.*

By HARRY HEPWORTH.

ALTHOUGH the action of the Grignard reagent on numerous types of organic compounds has been investigated, yet, with the single exception of the interaction of magnesium methyl iodide and methyl nitrate (Moureu, *Compt. rend.*, 1901, **132**, 837), no investigations have been carried out on the action of this important reagent on the nitric esters.

Moureu (*loc. cit.*) investigated the action of the Grignard reagent on certain nitroparaffins and esters of nitrous acid, and found that both classes of compounds gave rise to $\beta\beta$-dialkylhydroxylamines.

Bewad (*Ber.*, 1907, **40**, 3065) studied the action of magnesium or zinc alkyl iodides on esters of nitrous acid and on nitroparaffins. It was found that in the preparation of $\beta\beta$-dialkylhydroxylamines,

the zinc alkyl usually employed (*idem*, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 420, 455) can be replaced advantageously by zinc alkyl iodides or magnesium alkyl iodides when the esters of nitrous acid are used, but not in the case of nitroparaffins. With the latter, the reaction follows two courses, in both cases the final product being a $\beta\beta$-dialkylhydroxylamine, the one containing one alkyl group derived from the magnesium alkyl haloid employed, the other containing two.

From a consideration of the three possible structural formulæ for the esters of nitric acid, it is evident that, with the Grignard

$$\mathrm{RO{\cdot}O{\cdot}N{:}O} \qquad \mathrm{RO{\cdot}N}\begin{matrix}\nearrow\!\!\!\!=\mathrm{O}\\ \searrow\!\!\!\!=\mathrm{O}\end{matrix} \qquad \mathrm{RO{\cdot}N}\begin{matrix}\diagup\mathrm{O}\\ \diagdown\mathrm{O}\end{matrix}\!\!\Big|$$

reagent, a considerable number of reaction products can be theoretically anticipated. If Brühl's formula (the first) is correct, then it might be possible to obtain selective action of the Grignard reagent on one of the oxygen atoms attached to nitrogen. At the same time, primary selective action of the Grignard reagent with aromatic nitro-compounds, in which the nitro-group cannot possibly have a configuration as in the first formula, has been shown to take place by Oddo (*Atti R. Accad. Lincei*, 1904, [v], **13**, ii, 220), and confirmed by the author (T., 1920, **117**, 1004).

In an earlier communication (T., 1919, **115**, 1203), the author has shown that, in certain cases, selective action of the Grignard reagent can be easily realised by the application of the method of Kipping and Davies (T., 1911, **99**, 296). In this method, a mixture of the substance, together with alkyl haloid, diluted with ether, is added drop by drop to well-cooled ether containing magnesium powder, the rate of addition of magnesium being such as to keep the latter in excess throughout the reaction.

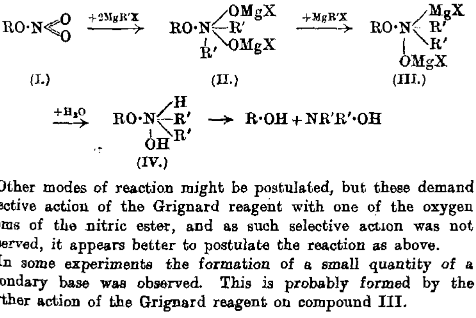
In this investigation, the action of magnesium methyl iodide and magnesium ethyl bromide on ethyl nitrate, ethylene glycol dinitrate, glyceryl trinitrate (nitroglycerol), and the tetranitro-derivative of pentaerythritol has been investigated. It was found that all these nitrates prevented the initial formation of Grignard compounds. This observation was repeatedly confirmed with small quantities of these nitric esters dried over phosphoric oxide for several days, and also with samples which had been first treated with a small quantity of a solution of the Grignard compound and then decanted. In other experiments, the formation of the Grignard compound was first started by the addition of a little alkyl haloid, and then the mixture of nitric ester and alkyl haloid was added, drop by drop, to the magnesium, but the vigorous reaction which was in progress soon ceased after a small portion of the nitric ester had been added, and could not be made to start

again. The only other observation of this type appears to be that recorded by Kipping and Davies (T., 1911, **99**, 296), who found that acetone prevented the interaction of magnesium and benzyl chloride or ethyl bromide.

It was therefore necessary to abandon this method of procedure and to prepare the Grignard reagent separately. Experiments were carried out under a variety of conditions, in which the nitric ester was added to the Grignard reagent and vice versa, and in which the reaction vessel was cooled to various temperatures from zero to $-15°$. In every case, the principal products of reaction were found to be either $\beta\beta$-dimethylhydroxylamine or $\beta\beta$-diethylhydroxylamine, whichever of the four nitric esters was employed. Minute traces of neutral products were formed, but the quantities obtained were not sufficient to admit of detailed examination.

The best results were obtained when three to four molecular proportions of the Grignard reagent to each $\cdot O\cdot NO_2$ group were employed.

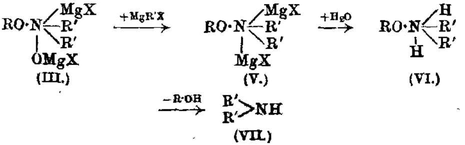
No selective action of the Grignard reagent was observed, and the course of the reaction, in the case of all four esters, may be simply represented as follows:



(I.) (II.) (III.) (IV.)

Other modes of reaction might be postulated, but these demand selective action of the Grignard reagent with one of the oxygen atoms of the nitric ester, and as such selective action was not observed, it appears better to postulate the reaction as above.

In some experiments the formation of a small quantity of a secondary base was observed. This is probably formed by the further action of the Grignard reagent on compound III.



(III.) (V.) (VI.) (VII.)

Bewad (*Ber.*, 1907, **40**, 3065) observed that nitric oxide was evolved, and secondary bases, as well as *ββ*-dialkylhydroxylamines, formed, on adding *iso*amyl nitrite to zinc ethyl iodide, and attributed both phenomena to a process of oxidation.

It is difficult to conceive how *ββ*-diethylhydroxylamine could be directly oxidised to diethylamine. In the course of the experiments described in this paper, it was observed that some nitric oxide was evolved when the flask was allowed to become hot during the decomposition of the product with water. The evolution of nitric oxide became more pronounced when the reaction product was distilled in steam, particularly at the early stages of distillation, or even when it was heated on the water-bath before the addition of water, and it is suggested that the nitric oxide is derived from the decomposition of the products III and V.

Exhaustive attempts were therefore made to isolate the bases by repeatedly extracting with ether, but even in those cases in which a very small quantity of water was used for the decomposition of the reaction product, eighteen to twenty extractions did not suffice to remove the whole of the bases present, so that, in spite of decomposition with evolution of nitric oxide during the early stages of the distillation with steam, the latter method of isolating the bases was more expedient and generally more satisfactory than extraction with ether.

EXPERIMENTAL.

Action of Magnesium Methyl Iodide on Ethyl Nitrate.

Preparation of Ethyl Nitrate.—The ethyl nitrate used in these experiments was prepared by a slight modification of the method of Lossen (*Ann. Suppl.*, 1868, **6**, 220). Nitric acid (D 1·4) of very low nitrous acid content was boiled for fifteen minutes with 1 per cent. of its weight of carbamide nitrate. After cooling, 100 grams of the acid were cautiously mixed with 100 c.c. of absolute alcohol in a retort connected with a condenser, and the contents of the retort evaporated to one-half of the volume on a sand-bath. A freshly prepared mixture of 100 grams of purified nitric acid and 50 c.c. of absolute alcohol was added drop by drop to the heated retort. Some considerable difficulty was encountered through this mixture becoming warm and fuming before it could be added, and a considerable improvement was effected by interposing a short water-condenser between the funnel and the retort. Distillation was continued until about two-thirds of the contents of the retort had passed over. The distillate was washed several times with water, dried over calcium chloride, and distilled from a salt-water

bath. The ethyl nitrate boiled constantly at 86°, and was kept over a little anhydrous sodium sulphate until required for use.

Reaction with Magnesium Methyl Iodide.—A mixture of 18·2 grams of ethyl nitrate and 50 c.c. of dry ether was added drop by drop to an ice-cold solution of magnesium methyl iodide, prepared in the usual way from 17·5 grams (3½ mols.) of magnesium, 102 grams (3½ mols.) of methyl iodide, and 250 c.c. of dry ether contained in a flask attached to a long reflux condenser. The ethyl nitrate–ether mixture was added during one hour, and reaction was just perceptible. After about two-thirds of the mixture had been added, the contents of the flask separated into two layers, the lower being of a green, oily consistence, and the upper distinctly milky. The flask was then removed from the ice and kept at the ordinary temperature for twenty-four hours, after which it was again cooled in ice, and the contents cautiously decomposed with 50 c.c. of cold water. With this quantity of water, the magnesium hydroxide separated as a stiff paste. During the decomposition, some nitric oxide was evolved, which was detected as nitrogen peroxide at the top of the condenser by the instantaneous action on a moistened starch–potassium iodide paper.

The contents of the flask were then distilled in steam until the condensed water no longer showed an alkaline reaction. The base was collected in hydrochloric acid. The solution, after being concentrated to a small bulk, was evaporated to dryness in a vacuum over sulphuric acid.

A small portion of the hydrochloride was recrystallised from a mixture of alcohol and ether, from which it separated in long needles. The compound softened at 92° and melted at 94—96° (Found: Cl=37·12, 37·08. $NMe_2{\cdot}OH,HCl$ requires Cl=36·41 per cent.). The hydrochloride therefore appears to be contaminated with the hydrochloride of some base of lower molecular weight.

Isolation of the base.—The crude hydrochloride was treated with an excess of a very concentrated solution of potassium hydroxide in a small flask attached to a condenser, and the base distilled into a receiver cooled in ice. A volatile, uncondensed base having an ammoniacal, fishy odour passed over first, then the temperature quickly rose to 90°, and a readily condensible base was collected, the greater portion at 93—95°, but the distillation was continued up to 100°. The liquid in the receiver, which was present in two layers, was shaken with 100 c.c. of ether and dried over barium oxide. On distillation, about 8 grams of crude product passed over at 91—96°, from which, on redistillation, 5 grams of a base boiling at 94·5—95·5° (corr.) were obtained. The com-

plete removal of the ether used for solution presented some difficulty.

The base had an unpleasant, ammoniacal odour. It quickly reduced Fehling's solution, especially on gently warming, and reduced an ammoniacal solution of silver nitrate instantly in the cold. It had D^{15} 0·8877, and was readily soluble in water, forming a solution with a strongly alkaline reaction (Found: N = 22·78, 22·82. C_2H_7ON requires N = 22·95 per cent.).

The base was reduced by tin and hydrochloric acid to dimethylamine, which was identified as its hydrochloride (Found: Cl = 43·48; N = 17·09. Calc.: Cl = 43·56; N = 17·18 per cent.).

The original base therefore appears to be ββ-dimethylhydroxylamine, as was suggested by Moureu (*loc. cit.*).

ββ-Dimethylhydroxylamine hydrochloride crystallises from alcohol or from a mixture of ether and alcohol in small, elongated, laminated plates melting at 102° (corr.). When crystallisation proceeds very slowly, the crystals are considerably more elongated than those deposited quickly. Its aqueous solution is acidic. It is readily soluble in ethyl or methyl alcohol, but almost insoluble in all other common organic solvents.

ββ-Dimethylhydroxylamine oxalate is most readily prepared by the addition of a clear, ethereal solution of anhydrous oxalic acid to an ethereal solution of two equivalents of the base. After keeping for two hours, the precipitated salt is thoroughly washed with dry ether and recrystallised from anhydrous methyl alcohol, from which it is deposited in small, hexagonal prisms melting at 154°. It is readily soluble in water, warm ethyl or methyl alcohol, sparingly so in hot acetone, and almost insoluble in all other common organic solvents (Found: N = 13·16, 13·14. $C_8H_{16}O_6N_2$ requires N = 13·20 per cent.).

This experiment indicated that traces of a base other than ββ-dimethylhydroxylamine were formed in the reaction, and further experiments were carried out in which 6 molecular proportions of magnesium methyl iodide were employed. The procedure was as described above, except that the volatile base first coming over on distillation was collected in dilute hydrochloric acid. By evaporation in a vacuum over sulphuric acid, about half a gram of crude dimethylamine hydrochloride was obtained. After two crystallisations from a mixture of ether and alcohol, the salt melted at 170°, and the melting point was not appreciably altered on mixing with a trace of pure dimethylamine hydrochloride. In this case, as before, the main product of the reaction was ββ-dimethylhydroxylamine.

Experiments were carried out in which the products of reaction

after decomposition with water, were extracted eighteen to twenty times with ether, and the base then converted into the hydrochloride. The yield in this case was not so satisfactory on account of the difficulty of extracting the whole of the base with ether.

Action of Magnesium Ethyl Bromide on Ethyl Nitrate.

A solution containing 18·2 grams of ethyl nitrate in 60 c.c. of dry ether was slowly added to magnesium ethyl bromide, prepared from 17·5 grams (3½ mols.) of magnesium, 80 grams (3½ mols.) of ethyl bromide, and 250 c.c. of ether, the flask being cooled to $-3°$. The reaction was very vigorous, much more so than in the case of magnesium methyl iodide.

After decomposition of the product with water (60 c.c.), the base was removed by distillation in steam, as in the previous experiment. The aqueous solution of the hydrochloride was concentrated in the water-bath, and finally in a vacuum over sulphuric acid. The free base was obtained as before, and the presence of some base of lower molecular weight again indicated.

The base (12 grams) boiled at 130—135°, with slight decomposition, reduced Fehling's solution on warming, and an ammoniacal solution of silver nitrate in the cold.

The oxalate was prepared by adding anhydrous oxalic acid to an ethereal solution of the base until no further precipitation took place. After recrystallising from methyl alcohol, the salt melted at 137—138°. The melting point of $\beta\beta$-diethylhydroxylamine oxalate is 136—137° (Dunstan, T., 1899, **75**, 793) or 138° (Wieland, *Ber.*, 1903, **36**, 2317).

The hydrochloride was prepared by treating an ethereal solution of the redistilled base with a solution of hydrogen chloride in the same solvent. The salt was extracted with a little water, and, after concentration of the aqueous solution in a vacuum over sulphuric acid, crystallised in long, colourless plates melting at 63—64° (Wieland, *loc. cit.*) (Found: Cl = 27·98. Calc.: Cl = 28·22 per cent.).

The base therefore appears to be $\beta\beta$-diethylhydroxylamine.

By treating ethyl nitrate with 6 molecular proportions of magnesium ethyl bromide, a small quantity of a volatile base, which boiled at 55—58°, was obtained, the hydrochloride of which melted at 217° (the mixture with diethylamine hydrochloride melted at 217—217·5°), from which it was evident that diethylamine was formed in this reaction.

Action of Magnesium Ethyl Bromide on Ethylene Glycol Dinitrate.

Preparation of Ethylene Glycol Dinitrate.—Thirty grams of ethylene glycol (b. p. 137—139°/90 mm.) were esterified with a mixture of nitric and sulphuric acids (HNO_3 = 40·00; H_2SO_4 = 58·85; HNO_2 = 0·15; H_2O = 1·00 per cent.) in a large beaker surrounded by a freezing mixture, the glycol being added at such a rate that the temperature was maintained at 10—12°. The ratio of acid to glycol was 7 to 1. Air stirring was continued for ten minutes after the glycol had been added, and the glycol dinitrate was then allowed to separate for thirty minutes, no accelerator being employed. After removing the mixed acid the glycol dinitrate was washed with water at 25°, with sodium carbonate solution (1 per cent.), again with water, and, after filtration, dried in a partial vacuum over solid potassium hydroxide. It was thus obtained as a clear, mobile, faintly yellow oil (D^{12} 1·480) (Found: N = 18·37, 18·41. Calc.: N = 18·42 per cent.) The yield was 55 grams.

Reaction with Magnesium Ethyl Bromide and with Magnesium Methyl Iodide.—A very vigorous reaction occurred when a mixture of 10 grams of ethylene glycol dinitrate and 30 c.c. of dry ether was added drop by drop during one hour to an ice-cold solution of magnesium ethyl bromide, prepared in the usual way from 12 grams (7 mols.) of magnesium and 54 grams (7 mols.) of ethyl bromide contained in a flask attached to a long reflux condenser. A greyish white solid quickly separated, and the upper layer became distinctly milky. After keeping at the ordinary temperature for twenty-four hours, the flask was again placed in ice, and its contents cautiously decomposed with cold water (60 c.c.), some nitric oxide being thereby evolved. The base was then distilled in steam and purified, as in the previous experiments.

Nine grams of a base, b. p. 132—137°, were obtained, the identity of which with $\beta\beta$-diethylhydroxylamine was established by its conversion into the hydrochloride, m. p. 63—64°, and oxalate, m. p. 137—139°.

After removal of the base, the ether contained a neutral product, the quantity of which, however, was too small for investigation.

In a similar experiment, in which 10 grams of the glycol dinitrate were added to a solution of magnesium methyl iodide prepared from 12 grams (7 mols.) of magnesium, 70 grams (7 mols.) of methyl iodide, and 250 c.c. of dry ether, 6 grams of $\beta\beta$-dimethylhydroxylamine were obtained, the identity of the base

being established by the b. p. and by its conversion into the hydrochloride and the normal oxalate. The reaction of the glycol dinitrate with magnesium methyl iodide is much less violent than with magnesium ethyl bromide.

Action of Magnesium Ethyl Bromide and of Magnesium Methyl Iodide on Glyceryl Trinitrate (Nitroglycerol).

Preparation of Glyceryl Trinitrate.—Thirty grams of glycerol were esterified in the same manner as ethylene glycol. The product was stabilised by washing successively with water at 25°, 1 per cent. sodium carbonate solution, and water, and, after filtration and drying in a vacuum over solid potassium hydroxide, yielded 62 grams of glyceryl trinitrate having a faintly yellow colour (Found: N=18·48, 18·49. Calc.: N=18·51 per cent.).

Reaction with Magnesium Ethyl Bromide and with Magnesium Methyl Iodide.—A mixture of 10 grams of glyceryl trinitrate and 60 c.c. of dry ether was added drop by drop to an ice-cold solution of magnesium ethyl bromide, prepared from 12·5 grams (11 mols.) of magnesium, 57 grams (11 mols.) of ethyl bromide, and 250 c.c. of dry ether. Nine grams of ββ-diethylhydroxylamine were isolated in the usual way.

In a similar experiment with a solution of magnesium methyl iodide, prepared from 75 grams of methyl iodide and the same quantity of magnesium as before, 6 grams of ββ-dimethylhydroxylamine were obtained from 10 grams of glyceryl trinitrate.

The reaction with magnesium ethyl bromide was again observed to be much more vigorous than with magnesium methyl iodide.

Action of Magnesium Ethyl Bromide and of Magnesium Methyl Iodide on Pentaerythritol Tetranitrate.

Pentaerythritol tetranitrate was prepared by Vignon and Gerin's method (*Compt. rend.*, 1901, **133**, 590). Eight grams of finely powdered pentaerythritol were added to 50 grams of nitric acid (97 per cent.) at 0°, the temperature being kept below 12° during the addition. At first the solution was clear, but the nitrate soon began to separate. The mixture was slowly added to 80 grams of concentrated sulphuric acid at 0°. After one hour, the product was collected, washed with water, dissolved in acetone, and precipitated with alcohol; it then melted at 138—139° (Found: N=17·53; 17·60. Calc.: N=17·72 per cent.).

Pentaerythritol tetranitrate is almost insoluble in ether. The solution obtained by shaking 1 gram of the substance with

1000 c.c. of dry ether for two to three hours was added to a solution of magnesium ethyl bromide, prepared from 1·2 grams of magnesium (14 mols.), 5 grams (14 mols.) of ethyl bromide, and 30 c.c. of dry ether. A small quantity of base was obtained, and its identity with $\beta\beta$-diethylhydroxylamine established by conversion into the hydrochloride and the oxalate.

In a similar manner, $\beta\beta$-dimethylhydroxylamine was obtained when magnesium methyl iodide was employed.

The author is indebted to the Reseatch Committee of Messrs. Nobel's Explosives Company, Ltd., and particularly to Mr. Rintoul, for the facilities accorded him in carrying out this investigation.

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[*Received, December 28th, 1920.*]

XXXI.—*The Melting Points of Mixtures of* o- *and* p-*Toluenesulphonyl Chlorides.*

By Leonard Harding.

In connexion with an investigation of the toluenesulphonyl chlorides, it became desirable to obtain accurate data concerning the melting points of mixtures of the ortho- and para-isomerides. This question has been investigated by Holleman (*Ber.*, 1911, **44**, 2504), but his method of preparing *o*-toluenesulphonyl chloride did not appear very satisfactory, and he did not directly determine the eutectic point. His data indicate that the eutectic temperature is in the neighbourhood of 1°, and the eutectic mixture contains between 15 and 25 per cent. of the *p*-sulphonyl chloride.

Preparation of o- *and* p-*Toluenesulphonyl Chlorides.*

Holleman prepared the *o*-sulphonyl chloride after fractional crystallisation of the mixed barium salts obtained from the sulphonation product of toluene. The following method seems preferable in ensuring the purity of the *o*-sulphonyl chloride. Pure *o*-toluenesulphonamide (m. p. 156°) is readily obtained by repeated fractional precipitation from a hot, approximately normal solution of derivative. A portion of the solution is titrated, and

the amount of acid required to precipitate the whole of the amide determined. After heating the main portion of the solution to 90°, a proportion of this amount of acid is slowly added, the proportion depending on the purity of the amide taken and the temperature at which the precipitate is filtered. Using an amide, m. p. 152—154°, and filtering at 65°, the amount of acid taken is 90 per cent. of that required for total precipitation. The pure amide is but very slowly hydrolysed by prolonged boiling with mineral acids or sodium hydroxide solution; the hydrolysis is completely effected by dissolving the amide (250 grams) in concentrated sulphuric acid (1100 grams), adding powdered sodium nitrite (110 grams) at 0°, and allowing the mixture to remain in the refrigerator overnight and at the ordinary temperature during the following day. The product is then poured into water, the solution neutralised with sodium hydroxide, evaporated to dryness, and the sodium *o*-toluenesulphonate extracted with boiling alcohol.

The *o*-toluenesulphonyl chloride, prepared by treating this salt with phosphorus pentachloride in the ordinary way, is purified by distillation under reduced pressure, and is thus obtained as a colourless liquid, b. p. 126°/21 mm., D_4^{20} 1·3383; after freezing, the substance melts at 10·17°. The refractive indices were determined at 17·2° by the hollow prism method, n_α 1·5528, n_D 1·5575, n_β 1·5713, and n_γ 1·5937; determinations made with the Pulfrich refractometer gave n_D^{20} 1·55653.

p-Toluenesulphonyl chloride was purified by repeated fractional crystallisation from light petroleum, followed by fractional distillation under reduced pressure; it melted at 67·2°.

The Melting-point Curve.

Mixtures of the two chlorides were weighed into a large test-tube fitted with a thermometer reading to 0·1°, and a suitable stirrer, precautions being taken to prevent access of water vapour; the test-tube was supported by a rubber fitting in a larger one suspended in a water-bath. After the mixture had been partly frozen by slow cooling, the bath was gradually heated, and the temperature at which the last fragments of crystal disappeared recorded as the melting point. The melting points of the different mixtures were determined several times, fresh mixtures being either made up anew or prepared by adding one or the other chloride to the mixture already contained in the tube.

When the results recorded in the following table were plotted on a curve, the eutectic temperature was found to be 1·6°. This was confirmed by measurements made on the eutectic mixture itself

and by the fact that, when completely frozen mixtures were gradually melted, a marked arrest on the temperature-time curve occurred at 1·6°. The eutectic mixture contained 17·5 per cent. of the para-isomeride.

p-Sulphonyl chloride, per cent.	M. p.	*p*-Sulphonyl chloride, per cent.	M. p.
0·0	10·17°	18·0	3·9°
2·0	9·9	19·0	6·6
5·8	8·0	20·0	7·9
8·0	7·0	25·0	14·7
10·0	5·8	29·1	20·2
12·0	4·9	35·3	26·9
14·0	3·8	42·2	33·6
15·0	3·0	50·2	39·8
16·0	2·6	56·2	44·1
17·0	2·1	62·8	48·4
17·25	1·9	68·8	51·9
17·5 eutectic	1·6	78·2	57·3
17·75	3·3	89 7	62·6
		100·0	67·2

I take this opportunity of thanking Professor Sir William J. Pope and Dr. Mills for their advice and criticism.

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XXXII.—*The Solubility of Ethyl Ether in Solutions of Sodium Chloride.*

By PERCY CYRIL LESLEY THORNE.

THE lowering of the solubility of ether in water by the presence of dissolved substances in the water has been known for a very long time. In particular, the addition of sodium chloride to aqueous liquids which are to be extracted with ether is commonly adopted as a measure of economy in the laboratory. Quantitative experiments on the precise effect of the addition of sodium chloride to the aqueous layer are, however, only occasionally met with in the literature (Euler, *Zeitsch. physikal. Chem.*, 1904, **49**, 303; Bennett, *Pharm. J.*, 1912, [iv], **35**, 146; Thorin, *Zeitsch. physikal. Chem.*, 1915, **89**, 685; Linde, *Arkiv. Kem. Min. Geol.*, 1917, **6**, No. 20, 1). It seemed desirable, therefore, in view of the practical importance of this particular system and of its possible theoretical interest, to determine the solubility of ether in salt solutions for a complete range of concentrations of sodium chloride.

EXPERIMENTAL.

Determinations of solubility were made at 15° and at 25° for a number of concentrations of sodium chloride.

The ether used was distilled, washed with a solution of potassium permanganate and then with water, dried for a week over powdered calcium chloride, and finally over sodium. It was then redistilled and kept over sodium. It was obviously more essential to exclude alcohol than water from the ether used, which gave no iodoform reaction and no hydrogen with sodium.

Twice-distilled water was used. The purest sodium chloride obtainable was recrystallised from water, and found to be neutral and free from calcium and magnesium, sulphates, etc.; a concentrated solution was made, and diluted as required.

About 150 c.c. of the salt solution were covered with an excess of ether in a stout, wide-mouthed bottle, which was then vigorously shaken mechanically in the thermostat. Equilibrium was found to be rapidly established under these conditions, but in all cases the shaking was continued for three and a-half to four hours. The temperature remained constant to 0·1°.

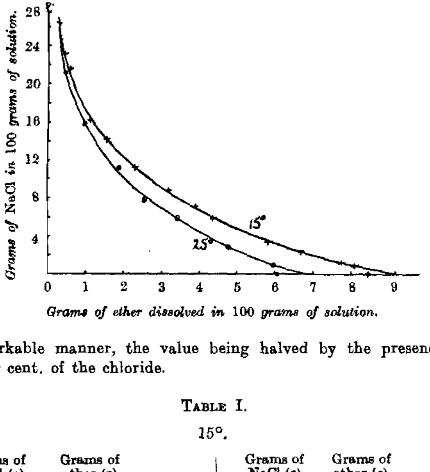
A sample was removed from the aqueous layer in the bottle by the following method. The stopper was replaced by a rubber bung fitted with two glass tubes, one passing just through the bung, the other, of narrower bore, reaching to the bottom of the bottle. The end of the longer tube was drawn out to a fine point and sealed, whilst outside the bottle this tube was bent twice at right angles. On inserting the bung, the fine point was broken by contact with the bottom of the bottle, thus admitting the aqueous layer uncontaminated by the ethereal layer. By blowing into the shorter tube, a quantity of the aqueous layer was forced over into the analysis apparatus.

The ether dissolved by the salt solution was estimated by transferring the sample to a small distillation flask containing about 10 c.c. of water, and attached at the side-tube to two U-tubes in series filled with calcium chloride. The whole apparatus was weighed before and after the addition of the sample, then dry air free from carbon dioxide was bubbled through the diluted sample by means of a long tube passing to the bottom of the flask. In this apparatus, the sample was thus immediately diluted to reduce the loss of ether, and the ether estimated by the loss in weight of the whole apparatus, when, after the passage of air for three to six hours, it had become constant.

The sodium chloride was estimated by diluting the liquid remaining in the flask and titrating a suitable volume with silver nitrate.

At least two samples were taken for analysis from each equilibrium mixture, generally on successive days. The results of the duplicate estimation did not vary by more than 2 per cent. of the weight of the ether. The mean is given in each case in the following tables, I at 15°, II at 25°. Both sets of results are plotted in Fig. 1. It can be seen that even small additions of sodium chloride to water decrease the solubility of ether in a

FIG. 1.



remarkable manner, the value being halved by the presence of 6 per cent. of the chloride.

TABLE I.

15°.

Grams of NaCl (c) in 100 grams of solution.	Grams of ether (s) in 100 grams of solution.	(s) Calc.	Grams of NaCl (c) in 100 grams of solution.	Grams of ether (s) in 100 grams of solution.	(s) Calc.
0·0	8·43 ($=s_0$)	9·16	8·750	3·20	2·99
*0·91	8·10	8·19	11·08	2·32	2·22
1·033	7·73	8·05	14·16	1·55	1·50
2·300	6·67	6·82	16·24	1·11	1·15
3·307	5·81	6·00	21·58	0·577	0·582
5·881	4·37	4·33	23·18	0·454	0·472
7·108	3·91	3·70	26·52	0·307	0·309

* Bennett (*loc. cit.*).

Fig. 2 is obtained by plotting the values of c and $\log_{10} s$ at both temperatures, and the fact that two straight lines are obtained

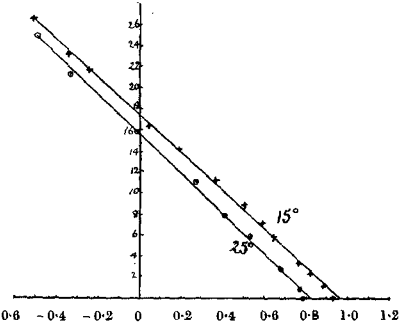
ndicates a relation of the form $\log s = a - kc$, where s is the solu-
ility of ether in brine of concentration c grams in 100 grams of
olution, k is a constant depending on the temperature and the
ature of the dissolved substance, a is a constant approximately
qual to $\log_{10} s_0$, where s_0 is the solubility of ether in pure water.
Replacing a by $\log_{10} s_0$, we have $\log s = \log s_0 - kc$, or

$$\frac{1}{c} \log \frac{s_0}{s} = k.$$

The constant k has the value 0·0555 at 15° and 0·0536 at 25°
hen logarithms to base 10 are used and concentrations expressed
n grams per 100 grams of solution. The solubilities of ether

FIG. 2.

Grams of NaCl *in* 100 *grams of solution.*



Log_{10} *(grams of ether dissolved.)*

TABLE II.

25°.

Grams of NaCl (c) in 100 grams of solution.	Grams of ether (s) in 100 grams of solution.	(s). Calc.	Grams of NaCl (c) in 100 grams of solution.	Grams of ether (s) in 100 grams of solution.	(s). Calc.
0·0	6·05	6·76	7·812	2·57	2·57
*0·91	5·96	6·04	11·08	1·88	1·72
2·837	4·78	4·76	15·79	0·979	0·963
5·970	3·41	3·24	21·18	0·463	0·495
			24·90	0·309	0·312

* Bennett (*loc. cit.*).

calculated from the equation are given in column 3 of tables I and II, and the agreement with the observed results is good, except at concentrations below 1 per cent.

This relation has not hitherto been recorded in reference to the system ether–sodium chloride–water. The less extensive values of Linde (*loc. cit.*), when similarly plotted, also give a straight line, but he does not suggest such a relation. Equations of a similar nature have, however, been deduced by several investigators when working with similar systems, for example, Setschenov (*Zeitsch. physikal. Chem.*, 1899, **4**, 117; *Ann. Chim. Phys.*, 1892, [vi], **25**, 226), with various salts and carbon dioxide; Bodländer (*Zeitsch. physikal. Chem.*, 1891, **7**, 308), with alcohol and sucrose; Euler (*Arkiv. Kem. Min. Geol.*, 1903, **1**, 133), with various salts and aniline; Knopp (*Zeitsch. physikal. Chem.*, 1904, **48**, 97), with various salts and hydrogen or nitrous oxide; Dawson (*J. Soc. Chem. Ind.*, 1920, **39**, 151T), with sodium sulphate and phenol. In these systems (except in the case of sucrose–alcohol–water), a non-electrolyte, a gas or liquid of comparatively low solubility, is expelled from the solution by an electrolyte which is fairly soluble. The converse case, in which a slightly soluble electrolyte is made less soluble by the addition of a non-electrolyte of considerable solubility, has been studied for many systems by Rothmund (*Zeitsch. Elektrochem.*, 1908, **14**, 532; *Zeitsch. physikal. Chem.*, 1909, **69**, 523), who found that a similar relation existed. He gives in his second paper a theoretical deduction of the logarithmic law in the two cases, stating it in the general form $\frac{1}{c}\log_e\frac{\eta_1}{\eta'_1} = \frac{a}{RT}$.

Hoffmann and Langbeck (*Zeitsch. physikal. Chem.*, 1905, **51**, 385) give two logarithmic expressions of greater complexity to summarise the results of their work on the alteration in solubility in water suffered by benzoic, *o*-nitrobenzoic, and salicylic acids on the addition of electrolytes and non-electrolytes, respectively.

A logarithmic relation of the type applicable to the salting out of ether appears, therefore, to express the equilibria in a large number of similar systems, and as it can be deduced thermodynamically, is preferable to merely empirical equations of more restricted utility.

The closely related results of some other workers have been plotted in similar fashion by the present author, and straight lines obtained in the following cases:

	Electrolyte.	Non-electrolyte.
Steiner (*Wied. Ann.*, 1894, (2), **52**, 275) ...	Sodium chloride	Hydrogen
Euler (*Zeitsch. physikal. Chem.*, 1904, **49**, 303)	Sulphuric acid	Ether
Kremann (*Monatsh.*, 1910, **31**, 275)	„ „	„
Linde (*Arkiv Kem. Min. Geol.*, 1917, **6**, No. 20, 1)	Sodium chloride	Ether
	Sodium acetate	„
	Sodium chloride	Ethyl acetate
	Sodium acetate	„ „

In no case does the straight line pass accurately through the point obtained for the solubility of the non-electrolyte in water, and the values for low concentrations, when given, do not lie on the line. Euler's values for the system ether–sulphuric acid–water are only given for three concentrations, and are therefore scarcely conclusive; those of Kremann for the same system at 0° range from 16·9 grams to 81·6 grams of sulphuric acid per 100 grams of dilute acid, and, with the exception of the solubility value for pure water, which is particularly distant from the theoretical point, and the value for 49·1 per cent. sulphuric acid, lie very near a straight line.

Without doubt, many other similar systems would give results in accordance with the general equation brought forward in this paper.

TABLE III.

Interpolated Values.

15°.			25°.		
Grams of NaCl (*c*) in 100 grams of solution.	Grams of ether (*s*) in 100 grams of solution.	Molecular hydration of NaCl (*H*).	Grams of NaCl (*c*) in 100 grams of solution.	Grams of ether (*s*) in 100 grams of solution.	Molecular hydration of NaCl (*H*).
0	8·43 (s_0)	—	0	6·05 (s_0)	—
1	8·06	[24·9]	1	5·98	[0·52]
2	7·09	[22·6]	2	5·28	[17·4]
4	5·49	25·1	4	4·13	22·6
5	4·84	24·4	5	3·65	22·6
6	4·26	24·1	6	3·22	22·1
8	3·30	21·5	8	2·52	20·5
10	2·65	19·4	10	1·97	18·7
15	1·35	15·0	15	1·11	14·4
20	0·71	11·6	20	0·57	11·5
25	0·37	9·2	25	0·31	9·1

In seeking for the cause of the lowering of solubility one comes, naturally, to the idea of hydration of the salt in solution. Taking as basis the suggestion of Philip (T., 1907, **91**, 711) that solvent thus attached to the solute is unavailable for the solution of a second solute, the molecular hydration of the sodium chloride has been calculated for the interpolated values given in table III. The water required to dissolve the observed quantity of ether was

calculated in each case from the solubility of ether in water, and the remaining water actually present was assumed to be used in hydrating the sodium chloride.

The values of H are given as molecules of water per molecule of sodium chloride, and are obtained by substitution in the expression

$$H = \frac{58 \cdot 5}{18}\left(\frac{100}{c} \cdot \frac{s_0 - s}{s_0} - 1\right).$$

The values obtained for the hydration at low concentrations of sodium chloride (below 4 per cent.) are obviously affected by other factors. For greater concentrations, the molecular hydration is considerably larger than that obtained by various methods by other workers. Thus Biltz (*Zeitsch. physikal. Chem.*, 1902, **40**, 220) obtained 19 and 25 as the hydrations of sodium chloride in $N/2$- and $N/10$-solutions, respectively, using the freezing-point method, and 14·5, 14·8, and 16·3 for $N/1$-, $N/2$-, and $N/4$-solutions, respectively, at 20° from the reduction in solubility of phenylthiocarbamide (*Zeitsch. physikal. Chem.*, 1903, **43**, 41).

The explanation may be that the ether is itself hydrated in aqueous solution.

It is hoped by wider application of the relations discussed in this paper to elucidate further the vexed problems of solution; work on the salting out of certain dyestuffs is now being carried on.

Summary.

(1) The solubility of ethyl ether in solutions of sodium chloride has been determined at 15° and at 25°. It decreases with increasing concentration of the salt.

(2) The logarithm of the weight of ether dissolved is found to vary directly with the concentration of sodium chloride, except in dilute solutions.

(3) The expression $\frac{1}{c} \log \frac{s_0}{s} = k$ holds, not only for this system, but for many other similar systems.

(4) The hydration of the sodium chloride has been calculated from these results.

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XXXIII.—*The Action of Ammonia on Acetone.*

By Thomas Stewart Patterson and Andrew McMillan.

In the course of the preparation of diacetonamine as an intermediate product in the synthesis of β-eucaine, acetone was saturated with ammonia four or five days in succession, and allowed to stand for about a fortnight or three weeks, the solution being then worked up for diacetonamine hydrogen oxalate. In the case of one preparation, however, it was noticed, after a rather cold night, that a crystalline substance had separated out, which at first was thought to be due to the bottle not having been properly cleaned. But on the following day, after another night colder than usual, the bottle was almost half full of this crystalline compound, which obviously could not be due to impurity. The crystals formed thin prisms one or two inches long. When some of the other preparations, which had been well saturated with ammonia, were cooled in a freezing mixture and a little of the solid compound was added, further large quantities of the substance crystallised out. Other preparations, from which nothing separated in this way, were again saturated with ammonia in the cold, and in a week or so the compound could easily be obtained from them also.

The properties of the new substance have been examined, and the following is a brief provisional account of the experiments which have been instituted and the results so far arrived at. It is communicated as a preliminary announcement for the purpose of claiming priority and the right to the further investigation of the subject.

The new compound is easily soluble in ether, but crystallises well from it, as also from benzene. It melts sharply at 45°, and volatilises very rapidly. It has a slightly basic smell (Found: N = 16·75 per cent.). On quick titration, 0·3946 gram of the substance, dissolved in water, required 22·6 c.c. of 0·1079*N*-hydrochloric acid to bring about the colour change with methyl-orange, but the solution quickly became alkaline again, and 42·2 c.c. of acid were required before a permanent end-point was reached.* In another experiment, 0·3944 gram of the base was dissolved in 50 c.c. of the above acid. The solution was then heated for a few minutes, and, on cooling, the excess of acid was titrated with

* To determine the strength of a solution of acetone which had been saturated with ammonia, Heintz (*Annalen*, 1877, 189, 214) added the alkaline solution to one of oxalic acid.

0·0565*N*-potassium hydroxide, 14·9 c.c. being required. It would appear from these results that there are two basic centres in the molecule, one being acted upon by hydrochloric acid much more rapidly than the other. Assuming that the base is di-acid, the molecular weight calculated from these two (complete) titrations is 173·7 and 173·2 respectively. $C_9H_{20}ON_2$ requires N = 16·28 per cent.; M = 172.

Some of the new compound was dissolved in ether, and dry hydrogen chloride was passed through the solution. A white, crystalline solid which separated was filtered off and dried. On analysis, this hydrochloride was found to contain 19·5, 19·2, 18·75 per cent. of chlorine, whereas the formula $C_9H_{20}ON_2$,HCl requires 17·11 per cent. It would therefore appear that hydrochloric acid is added on at one of the nitrogen atoms preferentially, and that the slightly high result is probably due to a small proportion of hydrogen chloride having been added on at the other nitrogen atom also. Taking all these results together, the most probable formula for the substance seems to be $CH_3·CO·CH_2·CMe_2·NH·CMe_2·NH_2$.

The hydrochloride precipitated from ethereal solution shows a peculiar behaviour when heated with alcohol. The hydrochloride goes into solution, but almost immediately a white precipitate separates out of the solution again. This precipitate on analysis, without special purification, gave figures lying somewhere between those for ammonium chloride and for methylamine hydrochloride, but the precipitate seemed too easily soluble in alcohol to be ammonium chloride. This point requires further investigation.

From these experiments, it was at first supposed that the new compound was formed on account of excessive saturation with ammonia, and that its formation was to be avoided in the preparation of diacetonamine hydrogen oxalate. The following experiment was therefore carried out. One litre of acetone was cooled in a freezing mixture and saturated with ammonia. The stopper of the bottle was tied in, and after ten days, when the smell of ammonia had almost entirely disappeared, this liquid was worked up for diacetonamine hydrogen oxalate, when 600 c.c. of the solution yielded 400 c.c. of recovered acetone and 400 grams of combined oxalates (ammonium, diacetonamine, etc.). This, on extraction with rectified spirit, gave 182 grams of insoluble residue (ammonium hydrogen oxalate, etc.) and 205 grams of diacetonamine hydrogen oxalate—not including a few grams still contained in the mother liquor.

By carrying out the process when the smell of ammonia had practically disappeared, it was expected that little or no ammonium oxalate would be produced. That this expectation is not realised

seems to show that when acetone is saturated with ammonia, it is not diacetonamine which exists in the solution, but probably in the first place $OH\cdot CMe_2\cdot NH\cdot CMe_2\cdot NH_2$, which then condenses with more acetone to yield the compound,

$$CH_3\cdot CO\cdot CH_2\cdot CMe_2\cdot NH\cdot CMe_2\cdot NH_2.$$

On treatment with oxalic acid, the latter substance decomposes, either at once or on heating, into diacetonamine hydrogen oxalate and ammonium oxalate, and possibly in other ways, in much the same manner as was mentioned above for the hydrochloride.

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XXXIV.—1 : 1-*Dimethyl*cyclo*hexane from Methylheptenone.*

By ARTHUR WILLIAM CROSSLEY and NORA RENOUF.

IN 1913, further work with hydroaromatic hydrocarbons was commenced, and as there seems no present possibility of completing the researches, it appears worth while to place on record the following brief account of certain points, which were definitely established in regard to 1 : 1 - dimethyl*cyclo*hexane during 1913—1914.

The hydrocarbon was first prepared in a pure condition in 1905 (T., **87**, 1487) from 1 : 1-dimethyldihydroresorcin as starting point, the main object of the investigation being to prove or disprove the identity of this substance with the hydrocarbon, C_8H_{16}, obtained by Zelinsky and Lepeschkin (*Annalen*, 1901, **319**, 303) from laurolene and *iso*laurolene, which they believed to be 1 : 1-dimethyl*cyclo*hexane.

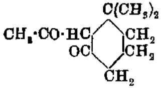
Zelinsky's hydrocarbon was proved not to be identical with 1 : 1-dimethyl*cyclo*hexane, and at a later date (T., 1906, **89**, 26) it was shown that dihydro*iso*laurolene is 1 : 1 : 2-trimethyl*cyclo*pentane and dihydrolaurolene is a mixture, the constituents of which were not definitely established.

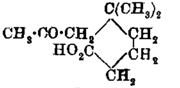
In 1913, Zelinsky and Lepeschkin (*J. Russ. Phys. Chem. Soc.*, **45**, 613) described experiments showing that 1 : 1-dimethyl*cyclo*hexane, "identical in properties with the hydrocarbon obtained by Crossley from dimethyldihydroresorcin," could be obtained from methylheptenone, and that the hydrocarbon so produced, when brominated, gave rise to tetrabromo-*p*-xylene. It has been frequently recorded that derivatives of 1 : 1-dimethyl*cyclo*hexane

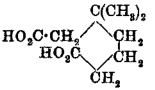
can be readily transformed into aromatic substances, which have, however, proved to be derivatives of *o*-xylene, and not *p*-xylene (T., 1904, **85**, 264; 1906, **89**, 875; 1908, **93**, 633; 1914, **105**, 165). It was therefore decided, in the first instance, to prepare some of the hydrocarbon from methylheptenone, and then to compare its properties with those of 1:1-dimethyl*cyclo*hexane.

Zelinsky indicates the reactions by which he obtained 1:1-dimethyl*cyclo*hexan-3-one from methylheptenone; the former of these two ketones can readily be converted into 1:1-dimethyl*cyclo*hexane, and therefore it follows that if the ketone can be obtained from methylheptenone, so also can the corresponding hydrocarbon.

There is no difficulty in preparing pure acetylmethylheptenone, $(CH_3)_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, from methylheptenone (Barbier and Leser, *Bull. Soc. chim.*, 1897, [iii], **17**, 748), but the conversion of the acetyl derivative into acetyldimethyl*cyclo*hexanone (I) under the influence of sulphuric acid (Leser, *Bull. Soc.*


(I.)


(II.)


(III.)

chim., 1899, [iii], **21**, 546) is a very complicated reaction, as, indeed, was realised by Leser in later communications (*Bull. Soc. chim.*, 1900, [iii], **23**, 370; 1902, [iii], **27**, 64; *Ann. Chim.*, 1912, **26**, 227). Leser in the last-quoted paper (*ibid.*, p. 243) recommended the use of pure commercial sulphuric acid (66°), but we have found that the best results are obtained by employing 80 per cent. acid, although even then the yield is small, amounting after the sodium bisulphite treatment to about 15 grams of acetyldimethyl*cyclo*hexanone from 116 grams of pure acetylmethylheptenone.

When hydrolysed with a 20 per cent. aqueous solution of potassium hydroxide in the cold, 16 grams of acetyldimethyl*cyclo*hexanone gave as principal product acetyldimethylhexoic acid (II), as was proved by the fact that, on oxidation, there resulted an almost quantitative yield of ββ-dimethylpimelic acid, melting at 102·5° (III).

Only 3 grams of a ketone were obtained, which was proved to be 1 : 1-dimethyl*cyclo*hexan-3-one (T., 1907, **91**, 81), because, on reduction with sodium in moist ethereal solution, it gave an alcohol, the *o*-nitrobenzoyl derivative of which melted at 62°, and this melting point was not lowered on admixture with the *o*-nitrobenzoyl derivative of 1 : 1-dimethyl*cyclo*hexan-3-ol (T., 1915, **107**, 604). Moreover, the ketone gave a liquid oxime, from which the benzoyl derivative was prepared, melting at 66—68°, but not becoming quite clear until 80°. Further fractionation from aqueous alcohol gave a pure substance melting at 91—92°, and this melting point was not altered on mixing with the benzoyl derivative of the oxime of 1 : 1-dimethyl*cyclo*hexan-3-one.

When the benzoyl derivative of the oxime of 1 : 1-dimethyl*cyclo*hexan-3-one was first described (T., 1907, **91**, 81), the melting point was given as 69°, which is incorrect. The notes made at the time show that this was not as sharp a melting point as the above statement indicates, and that the substance did not completely clarify until 80°. Fortunately, the original specimen, prepared in 1907, had been preserved, and it was found that, on further crystallisation from aqueous alcohol, a pure substance melting at 91—92° was produced.

These facts prove that 1 : 1-dimethyl*cyclo*hexan-3-one can be prepared from methylheptenone, and therefore the hydrocarbon obtained by Zelinsky and Lepeschkin (*ibid.*) in 1913 from methylheptenone was 1 : 1-dimethyl*cyclo*hexane. Though this is a fact of some considerable interest, this method is by no means to be recommended for the preparation of the hydrocarbon.

Zelinsky (*ibid.*) states that, when treated with bromine in presence of aluminium bromide, his hydrocarbon "gave very easily tetrabromo-*p*-xylene melting at 256°. As a control, the tetrabromide was prepared directly from *p*-xylene, and was found to melt at 256—257°, whilst a mixture of the two tetrabromides melted at the same temperature."

As already mentioned, in all cases noted by the present authors of the transformation of hydroaromatic substances into aromatic compounds necessitating the wandering of a methyl group, such group has always taken up an ortho-position relative to its original situation. It is true that in the dry distillation of the phosphate of 3 : 5-diamino-1 : 1-dimethyl*cyclo*hexane (T., 1909, **95**, 935), a meta-derivative was produced, but the cases are not strictly analogous, and, as suggested, if both methyl radicles in the *gem*-dimethyl group swing into ortho-positions, a meta-body would result.

For these reasons, it seemed essential to inquire further into

the suggested transformation of 1:1-dimethyl*cyclo*hexane into a derivative of *p*-xylene.

In the first instance, the tetrabromo-derivatives of *o*-, *m*-, and *p*-xylene were prepared by slowly adding the hydrocarbon to the theoretical quantity of bromine, to which a trace of iodine had been added. All three derivatives crystallised from purified commercial xylene in long, slender, glistening needles.

	Ortho.	Meta.	Para.
Melting points	257°	248°	249°
Resolidifying points ...	252°	241°	244°

The mixed melting points were found to be as follows:

Ortho + meta.	Ortho + para.	Meta + para.
250—252°	250—253°	247—249°

It is interesting to note that, in 1919, R. and W. Meyer (*Ber.*, **52**, [*B*], 1250) gave practically identical data regarding the melting points of these substances. In such instances, no very definite information can be gained from a consideration of the mixed melting points, but it is clear that the melting point of Zelinsky's tetrabromide (256°) corresponds more closely with the melting point of tetrabromo-*o*-xylene than with that of tetrabromo-*p*-xylene, and the ortho-derivative is the only one of the three which melts above 250°.

To test the point further, some pure 1:1-dimethyl*cyclo*hexane, prepared from dimethyldihydroresorcin, was brominated with bromine and aluminium bromide, as described by Zelinsky, but the melting point of the resulting tetrabromo-derivative (*A*) could not be raised above 252°. The following mixed melting points were obtained:

A + tetrabromo-*o*-xylene (257°), 254—256°,
A + tetrabromo-*m*-xylene (248°), 250—252°,
A + tetrabromo-*p*-xylene (249°), 250—252°,

from which it is seen that mixed melting-point determinations are useless for the purpose of identifying the tetrabromo-derivatives of the xylenes.

The reaction is a very drastic one, and possibly the explanation is similar to that suggested above as taking place in the dry distillation of the phosphate of 3:5-diamino-1:1-dimethyl*cyclo*hexane, where, in part, both groups in the *gem*-dimethyl radicle wander into ortho-positions, thus giving rise to a small amount of the meta-derivative, which slightly affects the melting point of the main product, namely, tetrabromo-*o*-xylene.

In a previous paper (T., 1905, **87**, 1498), it was stated that

when 1:1-dimethyl*cyclo*hexane was treated with a mixture of nitric and sulphuric acids, a nitrogenous substance was produced melting at 113—114°, but in amount too small for complete identification. At a later date (T., 1908, **93**, 646) it was shown that 1:1-dimethyl-$\Delta^{2:5}$-*cyclo*hexadiene gave, under the influence of nitric acid, small amounts of the two trinitro-*o*-xylenes, melting respectively at 71° and 115°, and it seemed that the above-mentioned substance migbt be one of the two trinitro-*o*-xylenes.

Twelve grams of pure 1:1-dimethyl*cyclo*hexane were therefore treated under the conditions already described, when a small amount of solid was produced, crystallising in transparent needles and melting at 115°; this melting point was not lowered on mixing with 3:4:5-trinitro-*o*-xylene (T., 1909, **95**, 211). The nitrogenous substance encountered in 1905 was evidently the same trinitro-*o*-xylene.

The original mother liquor from which the substance melting at 115° had separated was saturated with ammonium sulphate, when a further quantity of solid was obtained, which crystallised from dilute alcohol in transparent, flattened needles melting at 72°; this melting point was not lowered on mixing with 3:4:6-trinitro-*o*-xylene (T., 1909, **95**, 211).

There would not, therefore, appear to be any evidence of the production of a derivative of *p*-xylene from 1:1-dimethyl*cyclo*hexane or of the wandering of a methyl group in such reactions, other than ortho to its original position.

This work was carried out in the laboratories of the Pharmaceutical Society of Great Britain and of the University of London, King's College, during 1914.

[*Received, February* 14*th*, 1921.]

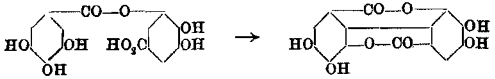
XXXV.—*Gallotannin. Part XII.**

By Maximilian Nierenstein, Charles William Spiers, and Arthur Geake.

Buchner (*Annalen*, 1845, **52**, 363) was the first to show that ellagic acid is formed when alkaline solutions of gallotannin are exposed to air. His observations were subsequently confirmed by Schiff (*Annalen*, 1873, **170**, 79; *Ber.*, 1879, **12**, 1534), Herzig

* Part XI.: Geake and Nierenstein, *Ber.*, 1914, **47**, 891.

and Broneck (*Monatsh.*, 1908, **29**, 248), Sisley (*Bull. Soc. chim.*, 1909, [iv], **5**, 727), and Trunkel (*Arch. Pharm.*, 1911, **248**, 202). The latter two considered the production of ellagic acid as experimental evidence for the presence of the *m*-digallic nucleus in gallotannin:



Both Sisley and Trunkel have to some extent overestimated the importance of their results, since ellagic acid is also produced from methyl gallate under identical conditions (Ernst and Zwenger, *Annalen*, 1871, **159**, 92; A. G. Perkin and Wilson, T., 1903, **83**, 133). We may therefore assume that the formation of ellagic acid from gallotannin proceeds either as suggested by Sisley and Trunkel, or in the manner by which ellagic acid is produced from the mononuclear methyl gallate.

Our observations seem to support the contentions of Sisley and Trunkel, for the following reasons: (1) If the oxidation of gallotannin is interrupted before the maximum amount of ellagic acid has been produced, a tannin-like residue is left. This residue (gallotannin residue *A*) contains no free ellagic acid, but gives ellagic acid, gallic acid, and dextrose on hydrolysis with dilute sulphuric acid. (2) The ellagic acid produced on hydrolysis of gallotannin residue *A* does not exist in the original gallotannin, but is formed during oxidation. Special emphasis must be laid on this point, since ellagic acid is a normal constituent of the tannin from Aleppo galls (Fischer and Freudenberg, *Ber.*, 1914, **47**, 2485) and Knopper galls (Nierenstein, T., 1919, **115**, 1174). Great care was therefore taken to establish with certainty the absence of ellagic acid in the specimen of Schering's tanninum levissimum purissimum I [purified according to Fischer and Freudenberg's method (*Ber.*, 1912, **45**, 915)] used by us during the whole investigation. For the detection of ellagic acid we used Fischer and Freudenberg's method, described by them in their research on Aleppo tannin (*loc. cit.*). (3) There is a distinct difference in the manner in which ellagic acid is produced from gallotannin and methyl gallate. Whereas the former gives rise only to ellagic acid, methyl gallate produces simultaneously ellagic acid and galloflavin, due to the formation of gallic acid by hydrolysis (compare Bohn and Graebe, *Ber.*, 1884, **20**, 2370).

During the present investigation, we have attempted a quantitative study of the production of ellagic acid from gallotannin.

Our results show that there are two distinct stages which underlie this process. The first stage produces a maximum of about 60 per cent. of ellagic acid; the second stage gives rise only to traces of ellagic acid, but yields about 8 per cent. of dextrose. These two stages do not synchronise, since the dextrose is mainly formed after all the ellagic acid has been produced. It therefore seems as if the dextrose is derived from a source which is only capable of producing little or no ellagic acid. This source (gallotannin residue *B*), which corresponds with about 30 per cent. of the gallotannin used, yields on hydrolysis with dilute sulphuric acid approximately 2 per cent. of ellagic acid, 9 per cent. of dextrose, and 84 per cent. of gallic acid.

We were at first inclined to regard these results as confirmatory evidence in favour of the pentadigalloylglucose formula of Fischer and Freudenberg (*Ber.*, 1912, **45**, 923). We assumed that the alkali removes at first, as in the case of penta-acetylglucose (Armstrong and Arup, T., 1904, **85**, 1043), four digalloyl residues, which would thus account for the first stage, during which ellagic acid is mainly formed. This stage is then followed by the elimination of the fifth digalloyl nucleus, which gives rise to the formation of little ellagic acid, the main product being dextrose (second stage).

This interpretation of the reaction clearly does not account for the production of gallotannin residue *B*, referred to above. To elucidate this point, the formation of ellagic acid from partly hydrolysed gallotannin [gallotannin residue *C*, prepared by acid hydrolysis according to Geake and Nierenstein's method (*Ber.*, 1914, **47**, 891)] was also studied. It seemed likely that gallotannin residue *C* would not yield the correspondingly large residue incapable of producing ellagic acid. At the same time, it seemed reasonable to expect that gallotannin residue *C*, that is, partly hydrolysed pentadigalloylglucose, would yield ellagic acid and dextrose simultaneously if our assumption was correct. This was, however, not the case. We again observed two distinct stages, which yielded, respectively, a maximum of about 45 per cent. of ellagic acid and 9 per cent. of dextrose. A residue (gallotannin residue *D*), which yielded only traces of ellagic acid, but mainly gallic acid and dextrose on hydrolysis with dilute sulphuric acid, was also obtained.

We consequently approached the question from another point of view. It seemed to us that if our previous assumption was correct, the methyl derivative of partly hydrolysed pentadigalloylglucose, that is, gallotannin residue *C*, should yield on hydrolysis partly methylated glucose. Gallotannin residue *C* was therefore

methylated with diazomethane, and subsequently hydrolysed with glacial acetic acid. Tetramethyl glucose was obtained, which again seemed contrary to our views and to the pentadigalloylglucose formula, since it was feasible to expect the formation of a less methylated glucose residue on hydrolysis.

As a check on these results, we extended the hydrolysis to methylogallotannin itself. Gallotannin was methylated with diazomethane (compare Herzig, *Ber.*, 1905, **38**, 989), and the methylo-derivative hydrolysed with glacial acetic acid, when we again obtained tetramethyl glucose. This unexpected result seemed to us so fundamentally opposed to Fischer's pentadigalloylglucose formula that we asked Prof. J. C. Irvine to examine our product. Prof. Irvine kindly undertook the investigation, and was able to establish the identity of our tetramethyl glucose.

From these results we are forced to one of two conclusions: (i) contrary to the pentadigalloylglucose formula for gallotannin, four hydroxyl groups of the glucose are free; (ii) the diazomethane has replaced the acyl groups, as observed by Herzig and Tischatschek (*Ber.*, 1906, **39**, 268, 1587) in the case of a few acetylated phenols. To check such a remote possibility as (ii), we have prepared pentagalloylglucose (Fischer and Bergmann, *Ber.*, 1918, **51**, 1760). This, on methylation with diazomethane and subsequent hydrolysis with glacial acetic acid, yielded glucose, and not tetramethyl glucose.

These observations reopen the question as to whether pentadigalloylglucose actually represents the constitution of gallotannin. It should be noted that Fischer's researches have not brought forward direct evidence in favour of his formula. All his deductions are of an entirely indirect character, and are based on the similarity—not the identity—of his synthetic products with gallotannin (compare Fischer, *Ber.*, 1913, **46**, 3253; 1919, **52**, 809; also Forster, T., 1920, **117**, 1177). It must also be borne in mind that we have no proof that gallotannin is a uniform product, even if purified according to Fischer's method. Thus, for example, Feist and Haun (*Arch. Pharm.*, 1913, **251**, 468) have shown that methylogallotannin from Fischer's purified gallotannin may be separated into three fractions containing, respectively, MeO = 30·7, 37·6, 33·2 per cent., whereas Iljin (*Ber.*, 1914, **47**, 895) has demonstrated that gallotannin having $[\alpha]_D + 75{\cdot}0^\circ$ in water [compare Fischer and Freudenberg (*Ber.*, 1912, **45**, 921), who find $[\alpha]_D^{20} + 72{\cdot}7^\circ$ in water for gallotannin purified according to their method] gives a series of fractions, where $[\alpha]_D$ is $+137{\cdot}8^\circ$, $+122{\cdot}1^\circ$, $+134{\cdot}3^\circ$, $+106{\cdot}6^\circ$, $+114{\cdot}8^\circ$, $+89{\cdot}1^\circ$, $+21{\cdot}8^\circ$, $+16{\cdot}4^\circ$.

Very few chemical problems have been so discouraging as the

chemistry of gallotannin. Since Scheele's first attempt in 1787 to prepare a pure "Galläpfelsalz" by a method which is, incidentally, similar to that employed by Fischer, the chemistry of gallotannin has been one long chain of disappointments. We find ourselves again faced with the necessity of regarding Fischer's pentadigalloylglucose formula and the advance for which it stands with reserve, if not with doubt, and we have consequently to consider the question as still open. In view of these facts, we publish our results without attempting to draw any conclusion as to the constitution of gallotannin. This seems to us the only feasible course at the present stage of the investigation, since we are now engaged in a revision of our previous researches on gallotannin, which were published during 1905—1914.

EXPERIMENTAL.*

Quantitative Observations on the Production of Ellagic Acid from Gallotannin.

The oxidations were carried out in measuring cylinders, moist air free from dust being aspirated through the alkaline solutions of gallotannin for a known length of time and at a constant temperature. The precipitates formed were collected in an alundum crucible, washed with distilled water containing a little ammonium carbonate, and subsequently treated with dilute hydrochloric acid (0·6 part in 20 parts). The ellagic acid thus formed was washed (i) with water acidulated with a few drops of hydrochloric acid, and (ii) with distilled water. It was finally dried to a constant weight at 150°. The alkaline filtrate and the first washings of the ellagic acid precipitates were quantitatively tested for dextrose by Fischer and Freudenberg's method (*Ber.*, 1912, **45**, 923), and the dextrose estimated volumetrically by Bertrand's method (*Bull. Soc. chim.*, 1906, [iii], **35**, 1286).

About fifty experiments were made at 20°, different concentrations of sodium hydroxide, carbonate and hydrogen carbonate, and also ammonia being used. The highest values were obtained in the case of a *N*/2-solution of sodium hydrogen carbonate. These gave an average of 59·3 per cent. of ellagic acid and 2·1 per cent. of dextrose after oxidation during forty-five hours, and 59·2 per cent. of ellagic acid and 2·2 per cent. of dextrose after oxidation during 110 hours. On raising the temperature to 40°, it was found that the oxidation was accelerated in such a manner that the production of dextrose was increased. Thus we found, when using a *N*/2-solution of sodium hydrogen carbonate, an average of 59·6

* All calculations are for anhydrous gallotannin.

per cent. of ellagic acid and 7·6 per cent. of dextrose after oxidation during thirty-two hours.

To ascertain if the ellagic acid is actually obtained from one particular source, the filtrate and first washings from the above-mentioned precipitates (gallotannin oxidised in $N/2$-sodium hydrogen carbonate at 8°) were acidified with dilute sulphuric acid. The liquid (about 140 c.c.) was extracted four times with 20 c.c. of ethyl acetate in order to remove any unoxidised tannin-like substance. The ethyl acetate extract was evaporated in a tared flask, and the residue (gallotannin residue) dried to a constant weight in a vacuum at 40°. Since, as may be seen from the following table, the quantity of ellagic acid increases as the gallotannin residue decreases, it seems probable that the latter is the main source from which the ellagic acid is formed.

Hours.	Ellagic acid. Per cent.	Gallotannin residue. Per cent.	Dextrose. Per cent.
4	13 3	91·4	0·2
6	38 8	57·4	0·8
12	52·9	11·5	1·1
16	55 9	10·3	—
24	58 4	2·0	2·1

Comparison between the Ellagic Acids from Gallotannin and from Methyl Gallate.

Several specimens of the crude ellagic acid obtained from gallotannin were analysed, without crystallisation from pyridine (compare A. G. Perkin and Nierenstein, T., 1905, **87**, 1412), and were found to give correct values (Found *: C=55·6, 55·4, 55·5, 55·7; H=2·3, 2·4, 2·1, 2·2. Calc.: C=55·6; H=2·0 per cent.). All specimens gave the Griessmayer test for ellagic acid (*Annalen*, 1871, **160**, 55; Perkin and Nierenstein, *loc. cit.*), and yielded on acetylation tetra-acetylellagic acid, which had the correct melting point (Found *: C=56·1; H=3·3. Calc.: C=56·2; H=3·0 per cent.).

The results obtained by analysing the crude ellagic acid from methyl gallate were not so satisfactory (Found *: C=54·7, 54·2; H=2·3, 2·4. Calc.: C=55·6; H=2·0 per cent.). On crystallisation from pyridine, correct values were, however, obtained (Found *: C=55·5, 55·3; H=2·4, 2·2 per cent.). It was also found that whereas the crude ellagic acid from methyl gallate did not give a clear Griessmayer reaction, the purified product behaved normally. Since it was also noticed that a trace of galloflavin (1:80) was sufficient to mask the Griessmayer test, it was thought

* Dried at 160°.

advisable to test the crude ellagic acid from both sources for this substance. Ellagic acid (42 grams) from methyl gallate was treated in the cold with a solution of 200 grams of sodium hydroxide in 2 litres of water, as described by Herzig and Wachsler (*Monatsh.*, 1914, **35**, 80) for the conversion of galloflavin into *iso*galloflavin. The *iso*galloflavin (2·7 grams) thus obtained was converted into tetramethyl*iso*galloflavin by means of an excess of diazomethane, and was found to melt correctly at 232—233° after several crystallisations from acetic acid and alcohol, animal charcoal being used each time (Found*: C=57·6; H=4·8. Calc.: C=57·5; H=4·2 per cent.). Two similar experiments with 30 and 36 grams of ellagic acid from gallotannin gave no trace of *iso*galloflavin.

Gallotannin Residue A.

Fifty grams of gallotannin dissolved in 5 litres of a $N/2$-solution of sodium hydrogen carbonate were oxidised for six hours. After removing the ellagic acid precipitate, the filtrate was acidified and extracted several times with ethyl acetate. On evaporation of the ethyl acetate, a brown solid (22 grams) remained, which, when dissolved in 150 c.c. of water, left only traces of an insoluble residue, probably ellagic acid. A 10 per cent. solution of lead acetate was added to the clear solution, and the precipitate decomposed with hydrogen sulphide. The filtrate was again extracted with ethyl acetate, and the residual solid purified in the same manner. The third ethyl acetate extract, diluted to 300 c.c. and dried over anhydrous sodium sulphate, gave, on addition of dry light petroleum, a bulky precipitate, which was collected, washed with light petroleum, and dried in a vacuum over paraffin. The product (18·5 grams) was then purified by Fischer and Freudenberg's method of purifying gallotannin. As a result, 16·8 grams of a colourless, amorphous product (gallotannin residue *A*) were obtained; a second preparation yielded 17·8 grams of the same product (Found †: C=53·4, 53·1; H=3·7, 3·9 per cent.). Gallotannin residue *A* precipitates gelatin and alkaloids, and gives all the colour reactions of gallotannin. Both preparations were optically active ‡:

Rotation in water (10 per cent. solution) $=[\alpha]_D^{16}$ +65·4°, +63·0°.
Rotation in alcohol (8 per cent. solution) $=[\alpha]_D^{18}$ +42·6°, +44·8°.
Rotation in acetone (8 per cent. solution) $=[\alpha]_D^{16}$ +27·8°, +26·4°.

* Dried at 160°.

† The same precautions with regard to moisture were taken as in the case of partly hydrolysed gallotannin (Geake and Nierenstein, *loc. cit.*, p. 897).

‡ For all rotations in this paper, L = 2·2, unless otherwise stated.

Two hydrolyses with dilute sulphuric acid according to Fische and Freudenberg's method gave: ellagic acid = 8·6, 7·2; galli acid = 84·2, 87·6; dextrose = 8·6, 9·1 per cent.

Gallotannin Residue B.

Two solutions of 50 grams of gallotannin in 5 litres of $N/2$ sodium hydrogen carbonate were oxidised for forty hours. Th filtered solution was acidified and extracted several times wit ethyl acetate to remove any gallotannin residue *A*. A 10 pe cent. solution of lead acetate was added to the aqueous layer, an the precipitate filtered. (The filtrate contained free dextrose 3·8 and 4·1 per cent. respectively.) The lead salt was decompose with hydrogen sulphide, the filtrate carefully neutralised wit ammonium carbonate, and evaporated under dimnished pressur (10—12 mm.). The residual solid was purified by several pre cipitations from absolute alcohol and dry light petroleum, an subsequently dried in a vacuum over paraffin. The two prepar ations gave 10·8 and 9·4 grams of an amorphous, slightly yello product, which precipitated gelatin and alkaloids, and gave all th colour reactions of gallotannin (Found *: C = 52·8, 52·2; H = 4·1 3·8 per cent.). Both preparations were optically active, bu showed some differences in their rotations:

Rotation in water (10 per cent. solution) $=[\alpha]_D^{16}$ +36·8°, +31·2°.
Rotation in alcohol (10 per cent. solution) $=[\alpha]_D^{16}$ +11·4°, + 8·6°.
Rotation in acetone (8 per cent. solution) $=[\alpha]_D^{21}$ +18·4°, +12·2°.

The two preparations were hydrolysed separately with dilut sulphuric acid according to Fischer and Freudenberg's method and gave: ellagic acid = 2·2, 2·3; gallic acid = 85·4, 83·6; dextrose = 8·4, 8·8 per cent.

Quantitative Observations on the Production of Ellagic Acid from Gallotannin Residue C.

These experiments were carried out in the same manner a those described in the case of gallotannin. Gallotannin residue *C* prepared by hydrolysis during four hours according to Geake and Nierenstein's method (*loc. cit.*), gave, when oxidised at 20° in $N/2$-sodium hydrogen carbonate solution, an average of 45·7 per cent. of ellagic acid and 2·2 per cent. of dextrose after oxidation during twenty-four hours, and 44·9 per cent. of ellagic acid and 2·7 per cent. of dextrose after oxidation during seventy-six hours

* The same precautions with regard to moisture were taken as in the cas of gallotannin residue *A*.

On raising the temperature to 40°, as in the case of gallotannin, it was found that the reaction was accelerated, the average production of ellagic acid becoming 44·6 per cent., and that of dextrose 6·2 per cent., after oxidation during thirty-two hours.

Gallotannin Residue D.

Forty grams of gallotannin residue *C*, dissolved in 5 litres of *N*/2-sodium hydrogen carbonate, were oxidised for forty hours, and the gallotannin residue *D* prepared exactly in the same manner as gallotannin residue *B*. The yield was 19·8 grams of an amorphous product, which resembled gallotannin in every respect (Found *: C=52·2; H=4·3 per cent.). The product was optically active:

Rotation in water (10 per cent. solution) $=[\alpha]_D^{16}+49{\cdot}6°$.
Rotation in alcohol (6 per cent. solution) $=[\alpha]_D^{18}+29{\cdot}4°$.
Rotation in acetone (8 per cent. solution) $=[\alpha]_D^{20}+12{\cdot}4°$.

On hydrolysis with dilute sulphuric acid, the following result was obtained: ellagic acid=0·3; gallic acid=92·4; dextrose=8·8 per cent.

Methylated Gallotannin Residue C.

An excess of diazomethane was allowed to act on the ethereal suspension of gallotannin residue *C* for twelve hours. As in the case of gallotannin (compare Herzig, *Monatsh.*, 1912, **33**, 843; Fischer and Freudenberg, *Ber.*, 1912, **45**, 2723), a residue insoluble in ether remained after methylation. The ethereal solution was filtered, evaporated to dryness, and the residue purified according to the method used by Herzig (*loc. cit.*) for the preparation of methylogallotannin. The amorphous product thus obtained had no definite melting point; it sintered at 52—57°, softened at 108—110°, and decomposed at 126—138°, thus resembling methylogallotannin (compare Fischer and Freudenberg, *loc. cit.*) [Found †: C=58·3, 58·5; H=4·7, 5·1 per cent.; compare Fischer and Freudenberg (*loc. cit.*, p. 2722), who found for methylogallotannin, C=58·62; H=4·88 per cent. Found †: MeO=37·4, 37·8, 37·2 per cent.; compare Herzig and Renner (*Monatsh.*, 1909, **30**, 543), who found for methylogallotannin, MeO=37·2 to 37·9 per cent.]:

Rotation in pyridine ‡ (10 per cent. solution) $=[\alpha]_D^{20}+9{\cdot}8°$.
Rotation in benzene ‡ (8 per cent. solution) $=[\alpha]_D^{18}+17{\cdot}8°$.

* The same precautions with regard to moisture were taken as in the case of gallotannin residue *A*.

† Dried over phosphoric oxide in a vacuum. ‡ *L* = 4·4.

Identification of Tetramethyl Glucose produced by Hydrolysis of Methylated Gallotannin Residue C *and Methylogallotannin.*

The following general procedure was adopted after many experiments. Ten grams of the methylo-derivative in question were dissolved in 50 c.c. of glacial acetic acid and heated in a sealed tube for eight hours at 160°. The contents of the tube were transferred to a flask, and the tube washed out several times with acetic acid. Water was then added and the precipitate filtered. The filtrate was concentrated under reduced pressure (8—10 mm.) to about one-eighth of the volume, and, after neutralisation with lead carbonate, precipitated with a 1 per cent. solution of lead acetate. The solution, after filtering, was saturated with hydrogen sulphide, filtered, and the hydrogen sulphide expelled by prolonged aspiration of air. The solution was freed from sulphur by filtering and shaking with a few c.c. of carbon disulphide, and evaporated to dryness in a vacuum (4—5 mm.). The residue was then dissolved in 10 c.c. of absolute alcohol, and again evaporated under diminished pressure to remove the last traces of acetic acid. The latter treatment was repeated several times, and the flask, which now contained a semi-solid mass, transferred to a vacuum desiccator containing paraffin. After remaining in the desiccator for 8—10 days, the product was extracted with boiling light petroleum until only traces of an oily residue remained. The solid left on evaporation of the light petroleum was dried for twenty-four hours in a good vacuum, and then purified according to the following method, which was kindly suggested to us by Prof. Irvine. It was first boiled under reflux with a quantity of dry light petroleum sufficient to dissolve approximately one-half of the material. The extract generally yielded a product of low melting point (*A*), which was impure, and crystallised after some time in needles, which did not melt sharply (the melting point of *A* was generally 58—71°, but on one occasion a product melting at 79—81° was also obtained). The solid remaining after extraction with light petroleum was dissolved in a fresh quantity of the same solvent, and the solution kept overnight, when tetramethyl α-glucose separated in long, delicate needles. This product melted at 94—96°, and the melting point was not depressed by admixture with tetramethyl α-glucose prepared in the same manner from a specimen of tetramethyl glucose sent to us by Prof. Irvine. The *yields thus obtained were 0·48 to 0·52 gram of tetramethyl* α-glucose from 10 grams of methylated gallotannin residue *C* and 0·38 to 0·41 gram from 10 grams of methylogallotannin. A further quantity of 0·18 to 0·22 gram was obtained by drying the

previously mentioned fraction A in a good vacuum, and repeating the whole process of purification with light petroleum * (Found †: C=50·6,‡ 50·4,‡ 50·7,§ 50·6,§‖ 50·7 §; H=8·8,‡ 8·7,‡ 8·7,§ 8·7,§‖ 8·6 §; OMe=52·5,‡ 52·3,§ 52·5.§ Calc.: C=50·8; H=8·5; OMe=52·6 per cent.).

The properties of the tetramethyl glucose obtained showed good agreement with those ascribed to it by Purdie and Irvine (T., 1903, **83**, 1032). Thus the optical rotation in alcohol of a specimen melting at 87—88° was $[\alpha]_D^{20}$ +76·8°; Purdie and Irvine give $[\alpha]_D^{20}$ +78·2°. At the suggestion of Prof. Irvine, we also prepared the tetramethyl glucoseanilide (Irvine and Moodie, T., 1908, **93**, 103; Irvine and Gilmour, *ibid.*, p. 1440). Our product (Found: N=4·8. Calc.: N=4·5 per cent.) melted at 131—133° (Irvine and Moodie give m. p. 135°). We found $[\alpha]_D^{20}$ +212·3° for the anilide after four crystallisations, whereas Irvine and Gilmour give $[\alpha]_D^{20}$ +224° for a specimen crystallised eight times. Our preparation showed the same rapid mutarotation observed by Irvine and Gilmour, since the addition of a trace of hydrogen chloride to the methyl-alcoholic solution produced a permanent value $[\alpha]_D^{20}$ +45·8° in twenty minutes, the corresponding value obtained by Irvine and Gilmour being $[\alpha]_D^{20}$ +47°.

Identification of Dextrose produced by the Hydrolysis of Fischer and Bergmann's Methylated Pentagalloylglucose.

Eight grams of pentatrimethylgalloyl-α-glucose,** which had been prepared according to Fischer and Bergmann's method (*Ber.*,

* These results have no claim to quantitative accuracy, and can only be accepted as qualitative observations. We now intend to study the estimation of tetramethyl glucose by a method similar to that elaborated by Bertrand for the estimation of glucose. By this method we hope later on to be able to carry out a quantitative research on methylogallotannin with reference to tetramethyl glucose and the other disintegration products.

† Dried in a vacuum over paraffin.

‡ From methylated gallotannin residue C.

§ From methylogallotannin.

‖ This product has not been purified by Professor Irvine's method. It melted at 83—85°, and was a mixture of the α- and β-forms.

** The optical rotations of this substance and of the intermediary products were taken for comparison with those obtained by Fischer and Bergmann for these amorphous substances. The values found for approximately the same concentrations were: (1) Penta(triacetylgalloyl)-α-glucose, $[\alpha]_D^{20}$ +43·1° in s-tetrachloroethane; Fischer and Bergmann give $[\alpha]_D^{22}$ +42·7°, and $[\alpha]_D^{15}$ +46·9°. (2) Pentagalloyl-α-glucose, $[\alpha]_D^{18}$ +78·4° in alcohol; Fischer and Bergmann give $[\alpha]_D^{18}$ +76·4° and +81·5°. (3) Penta(trimethylgalloyl)-α-glucose, $[\alpha]_D^{18}$ +64·8° in s-tetrachloroethane; Fischer and Bergmann give $[\alpha]_D^{20}$ +67·01°.

1918, 51, 1779), were hydrolysed with glacial acetic acid, as previously described. The dextrose was estimated in several portions of the hydrolysate after dilution to 100 c.c. (Found: dextrose = 14·2, 13·9, 14·2. Calc.: dextrose = 15·6 per cent.). The greater part was converted into the osazone, which crystallised from dilute alcohol in glistening, yellow needles melting at 203—204°; a mixed melting point with an authentic specimen of glucosazone showed no depression (Found: N = 15·7. Calc.: N = 15·6 per cent.).

We take this opportunity of thanking Prof. Irvine for his valuable advice and assistance during this investigation. We also wish to thank Mr. Robert Barr, B.Sc., for the many optical observations mentioned in this paper. Our thanks are also due to the Research Fund Committee of the Chemical Society and the Colston Society of the University of Bristol for grants which have covered the expenses of this research.

The University,
Bristol. [*Received, February 1st, 1921.*]

XXXVI.—*The Condensation of* m-*Dimethylaminophenol with Benzaldehyde.*

By Sri Krishna and Frank Geo. Pope.

This communication is a continuation of earlier work on the interaction of aldehydes and phenols, with the object of obtaining fluorone derivatives. In the earlier work, hydroxyfluorones were prepared, and it is hoped now to compare these with fluorones containing a basic group. With this object in view, the dimethylamino-hydrol has been prepared as a preliminary, and its chief derivatives described.

The *m*-dimethylaminophenol used was the commercial product, which was purified by distillation under 100 mm. pressure, and in this way obtained as a colourless, crystalline mass. On account of the ease with which a pink, and ultimately a dark red, coloration is produced, apparently by oxidation, it has been impossible to describe the various derivatives as colourless, whilst on attempted crystallisation many separate more or less in the condition of a scale preparation. On this account, the majority were dissolved in a suitable solvent, precipitated by the addition of

water or other solvent, and finally dried, in most cases in a vacuum over sulphuric acid.

Experimental.

4-*Dimethylamino-2-hydroxybenzhydrol*, $NMe_2 \cdot C_6H_3(OH) \cdot CHPh \cdot OH$.

The hydrol was obtained by dissolving 13·7 grams of *m*-dimethylaminophenol in 400 c.c. of 10 per cent. sodium hydroxide solution, and adding 10·6 grams of benzaldehyde. The mixture was well shaken and allowed to remain for seventy hours, by which time the odour of benzaldehyde had disappeared, and the solution had become dark red. The hydrol was precipitated by carbon dioxide as a pink solid. It was filtered, washed, dried, dissolved in ether, and precipitated by light petroleum, when it separated as an almost colourless solid, which, however, rapidly assumed a pink colour on keeping (Found: C=73·92; H=7·09; N=5·93. $C_{15}H_{17}O_2N$ requires C=74·07; H=6·99; N=5·76 per cent.). It is soluble in almost all the ordinary organic solvents, and melts at 146°.

The *potassium* salt was obtained as a dark red scale by dissolving the hydrol in the calculated amount of potassium hydroxide and concentrating the solution on the water-bath (Found: K=13·78. $C_{15}H_{16}O_2NK$ requires K=13·93 per cent.).

The *hydrochloride* was obtained by dissolving the hydrol in the calculated amount of acid and concentrating the solution, when it separated as a red powder decomposing at 138° (Found: Cl=12·70. $C_{15}H_{17}O_2N,HCl$ requires Cl=12·68 per cent.).

An *acid oxalate* was obtained by dissolving the hydrol in a solution of oxalic acid (1 equiv.). On concentrating the solution, it separated as a dark-coloured powder, which decomposed at 93° (Found: C=61·66; H=5·94. $C_{15}H_{17}O_2N,H_2C_2O_4$ requires C=61·81; H=5·74 per cent.).

The *dibromo*-derivative was prepared by dissolving the hydrol in glacial acetic acid and adding the calculated quantity of bromine, also dissolved in glacial acetic acid. The mixed solutions were heated on the water-bath for a few minutes, and the whole poured into water, when an orange-red precipitate was obtained, which was collected, washed, and dried. The substance decomposes when heated above 250°, and is soluble in alcohol (Found: Br=39·96. $C_{15}H_{15}O_2NBr_2$ requires Br=39·89 per cent.).

The *acetyl* derivative was prepared by heating 5 grams of the hydrol with 25 grams of acetic anhydride and 5 grams of anhydrous sodium acetate for three hours under reflux. The solution was

then poured into dilute alcohol and digested on the water-bath until the odour of the anhydride had disappeared. The solid product was collected, washed, dried, and recrystallised from alcohol, when it separated as a very pale brown, microcrystalline powder melting at 70° (Found: C=71·40; H=6·72; N=5·15. $C_{17}H_{19}O_3N$ requires C=71·58; H=6·67; N=4·91 per cent.).

The *benzoyl* derivative was prepared by dissolving 4·86 grams of the hydrol in a solution of the calculated amount of sodium hydroxide, and adding 2·8 grams of benzoyl chloride. The mixture was well shaken, and then poured into water, when the benzoyl derivative separated as a pale brown powder melting at 73° (Found: C=75·92; H=6·15. $C_{22}H_{21}O_3N$ requires C=76·08; H=6·05 per cent.).

6-Dimethylamino-3-hydroxy-9-phenylxanthen,

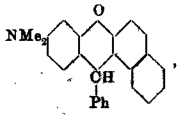
$$NMe_2\cdot C_6H_3 < \begin{matrix} O \\ CHPh \end{matrix} > C_6H_3\cdot OH.$$

4·86 Grams of the hydrol were heated with 2·2 grams of resorcinol and 6 grams of anhydrous zinc chloride for four hours at 170°. The mixture was then poured into dilute hydrochloric acid and heated for some time to remove zinc chloride. The dark brown mass was collected, washed, dissolved in glacial acetic acid, and precipitated by the addition of water, when it separated as a brown powder (Found: C=79·21; H=6·24; N=4·28. $C_{21}H_{19}O_2N$ requires C=79·49; H=5·99; N=4·42 per cent.).

The *benzoyl* derivative of the xanthen was obtained in the usual manner by the Schotten-Baumann reaction as a pale brown solid melting at 71—72°. The colour deepened rapidly on exposure to the air (Found: C=80·31; H=5·57. $C_{28}H_{23}O_3N$ reqnires C=79·81; H=5·47 per cent.).

6-Dimethylamino-3-hydroxy-9-phenyl-2-methylxanthen was prepared in a similar manner by the condensation of the hydrol with *p*-cresol. It was readily soluble in acetic acid, and, on dilution of the solution with water, separated as a brown powder, which melted at 98° (Found: C=83·61; H=6·63. $C_{22}H_{21}ON$ requires C=83·81; H=6·66 per cent.).

8-Dimethylamino-11-phenyl-β-naphthaxanthen,



obtained similarly by the condensation of the hydrol with β-naphthol, is readily soluble in glacial acetic acid, from which it separates as a brown powder melting at 105° (Found: C = 85·59; H = 6·17. $C_{25}H_{21}ON$ requires C = 85·47; H = 5·98 per cent.).

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(University of London). [Received, February 16th, 1921.]

XXXVII.—*Phenolcitraconein.*

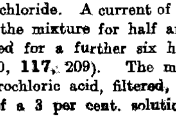
By Sri Krishna and Frank Geo. Pope.

Some years ago, one of us (F.G.P.), in conjunction with J. T. Hewitt, obtained in the preparation of citraconfluorescein a very small quantity of a by-product. This compound appeared, from the results of its analysis and from its properties, as far as they could be ascertained, to be a dihydroxybenzoylcrotonic acid, $C_6H_3(OH)_2{\cdot}CO{\cdot}C_3H_4{\cdot}CO_2H$. Lack of material and pressure of other work at the time prevented further examination of the acid.

Citraconic anhydride is now being condensed with various phenols in the hope that, by the decomposition of the resulting substances, acids of the above type may be obtained and characterised. In this preliminary communication, the preparation and properties of the simple phenolcitraconein are described.

Experimental.

Phenolcitraconein,



This substance was prepared by heating at 120° 20 grams of freshly distilled phenol, 10 grams of citraconic anhydride, and 10 grams of freshly fused zinc chloride. A current of dry hydrogen chloride was passed through the mixture for half an hour, after which the mixture was heated for a further six hours at 120° (compare Copisarow, T., 1920, **117**, 209). The melt was then heated with very dilute hydrochloric acid, filtered, washed, and finally extracted by means of a 3 per cent. solution of sodium

hydroxide. The red solution thus obtained was precipitated by the addition of dilute hydrochloric acid, when the citraconein was obtained as a brown precipitate. This was collected, washed, dissolved in alcohol, and reprecipitated by the careful addition of water. It separated as a light brown powder, m. p. 159—161°, readily soluble in alcohol, ether, and chloroform (Found: C=72·22; H=5·11. $C_{17}H_{14}O_4$ requires C=72·34; H=4·96 per cent.).

Phenolcitraconein dissolves readily in aqueous solutions of the alkali hydroxides, yielding red solutions, which are fainter in colour than similar solutions of phenolphthalein. The colour of the alkaline solution is discharged hy the addition of acids or by the use of an excess of alkali. In the latter case, however, the colour reappears on acidification, even if the alkaline solution has been previously boiled.

The *potassium* salt was obtained as a "scale" by dissolving the citraconein in the calculated amount of potassium hydroxide, previously dissolved in water, and concentrating the red solution (Found: K=21·97. $C_{17}H_{12}O_4K_2$ requires K=21·78 per cent.).

A *tetrabromo*-derivative, $C_{17}H_{10}O_4Br_4$, was obtained when a solution of bromine in glacial acetic acid was gradually added to a solution of the citraconein in the same solvent. The mixed solutions were heated on the water-bath for half an hour, and then poured into water, when an orange-yellow precipitate was obtained. This was collected, washed, and dried in the usual manner. It was soluble in ether, chloroform, and benzene, and melted at 189° (Found: Br=53·30. $C_{17}H_{10}O_4Br_4$ requires Br=53·51 per cent.).

The *diacetyl* derivative was obtained by heating 5 grams of the citraconein with 20 grams of acetic anhydride and 5 grams of sodium acetate for two hours. The mixture was then poured into dilute alcohol, and the whole digested on the water-bath until the excess of acetic anhydride was destroyed. The solid was collected, washed, boiled a second time with water, and finally crystallised from alcohol, from which it separated as a very light brown, microcrystalline powder melting at 134° (Found: C=68·73; H=5·11. $C_{21}H_{18}O_6$ requires C=68·85; H=4·91 per cent.).

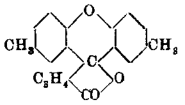
The *dibenzoyl* derivative was prepared by the Schotten-Baumann method. The crude product was dissolved in acetone, and the solution filtered into an excess of benzene, when the dibenzoate separated as a nearly colourless precipitate melting at 99° (Found: C=75·45; H=4·63. $C_{31}H_{22}O_6$ requires C=75·92; H=4·69 per cent.).

The *dimethyl ether*, $C_{19}H_{18}O_4$, was prepared by dissolving 5·6

grams of the citraconein in the calculated quantity of potassium hydroxide, previously dissolved in aqueous methyl alcohol, and adding 5 grams of methyl sulphate. The mixture was heated on the water-bath for two hours, and then faintly acidified. The brown solid obtained was collected, washed, dissolved in alcohol, and the solution poured into water, when the ether separated as a brown powder melting at 135° (Found: C=73·46; H=5·62. $C_{19}H_{18}O_4$ requires C=73·54; H=5·80 per cent.).

The *diethyl ether*, $C_{21}H_{22}O_4$, was prepared by dissolving the citraconein in a solution of the calculated amount of potassium hydroxide, adding 6·2 grams of ethyl iodide, and heating the whole under reflux for two hours on the water-bath. The solution was poured into water, the precipitate collected, washed, and dried. The substance is soluble in ether, chloroform, and acetic acid, and melts at 132° (Found: C=74·31; H=6·49. $C_{21}H_{22}O_4$ requires C=74·55; H=6·50 per cent.).

A *fluoran* derivative of citraconic anhydride was prepared by heating 4·3 grams of *p*-cresol with 2·2 grams of the anhydride and 3 grams of zinc chloride, and treating the product as described



under the citraconein. It is a light grey solid, m. p. 128—129°, which is insoluble in the alkali hydroxides, but dissolves readily in alcohol (Found: C=77·95; H=5·64. $C_{19}H_{16}O_3$ requires C=78·08; H=5·47 per cent.).

In conclusion, we desire to express our thanks to the firm of Messrs. Thos. Morson and Son for placing the necessary citraconic anhydride at our disposal.

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(UNIVERSITY OF LONDON). [*Received, February* 16*th*, 1921.]

XXXVIII.—*Additive Compounds of Antipyrylaminodiacetic Acid and its Salts with Neutral Salts.*

By ROBERT GEORGE FARGHER and HAROLD KING.

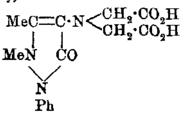
THE capacity of the weakly basic substance antipyrine to form additive compounds with very varied organic substances, generally containing oxygen, and with metallic salts of organic and inorganic acids, has often come to light in attempts to explain its incompatibility in pharmacy and to modify or supplement its action in therapeutics.

Apart from two compounds with calcium chloride,

$$(C_{11}H_{12}ON_2)_3,CaCl_2,12H_2O$$

and $(C_{11}H_{12}ON_2)_3,2CaCl_2,9H_2O$, described by Pfeiffer and Wittka (*Ber.*, 1915, **48**, 1289), no complexes are known with the haloids of the alkali or alkaline earth metals.

A simple derivative of antipyrine, antipyryl-4-aminodiacetic acid (D.R.-P. 144393),



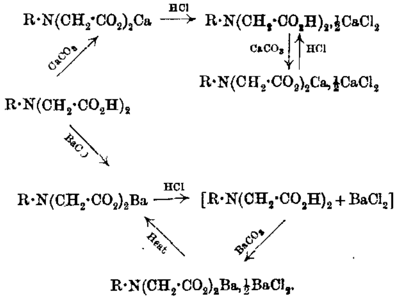
has been found by the authors to furnish an unusually interesting series of simply molecular, additive compounds with the haloids of the alkali and alkaline earth metals. Though the salts of this acid are dismissed in the original specification with the statement that the barium salt was obtained only as a hard, dry mass, the authors have found that the calcium, strontium, and barium salts are well-defined, crystalline substances containing various proportions of water of crystallisation, and have isolated, but with greater difficulty, crystalline sodium and potassium salts.

Additive compounds of two molecules of the acid with one of calcium chloride, calcium bromide, or strontium chloride, and of one molecule of the acid with one of sodium, lithium, or potassium chloride, have been prepared, but the analogous compounds from magnesium or barium chloride were not obtained.

The combining power is, moreover, retained by the calcium, strontium, barium, and magnesium salts of the acid, two molecules of the salt uniting with one of the corresponding metallic chloride.

The mode of preparation of these complexes is sufficiently indicated in the experimental portion of the paper. Attention

may, however, be drawn to the ease with which their formation and isolation can be realised experimentally. The following diagram shows the behaviour of the calcium and barium salts, where R represents the antipyryl group:



A satisfactory interpretation of the mode of attachment is a much more difficult matter. The authors believe that it is conditioned by the keto-group of the pyrazolone nucleus. The capacity of antipyrine and of antipyrylaminodiacetic acid and its salts to form complexes is evidently inherent in the pyrazolone nucleus, and, adopting the usual single-ring structure for this nucleus rather than the Michaelis bridged structure, the two seats of residual affinity are the tervalent methylated nitrogen atom and the oxygen of the carbonyl group. The calcium and lithium haloids are known to form complex ammines with ammonia, but only in the dry state. With bivalent oxygen compounds, however, the additive products with the alkali and alkaline earth metal haloids are very numerous, many of them crystallising from aqueous solution. Of these, the most thoroughly investigated (by Pfeiffer and his co-workers; also King and Palmer, *Biochem. J.*, 1920, **14**, 574) are the addition products of neutral salts with glycine and such simple derivatives of glycine as glycylglycine, sarcosine, betaine, and alanine. Pfeiffer and Wittka (*loc. cit.*) consider the neutral salt to be attached to the carbonyl group of the cyclic form of these substances, no other representation being possible for betaine. On this basis, the glycine–calcium chloride complex is represented thus, $(\overline{NH_2 \cdot CH_2 \cdot CO \cdot O})_2 \ldots CaCl_2$. In agreement with this, they observed that diketopiperazine united additively with two molecules of lithium chloride or bromide.

Moreover, the deep blue colour of copper glycine is usually interpreted by the cyclic structure

$$CH_2<\begin{matrix}CO_2^-\\NH_2\end{matrix}>Cu<\begin{matrix}CO_2^-\\NH_2\end{matrix}>CH_2$$

and it retains this structure, as shown by the colour, when it combines with a molecule of calcium chloride. The copper salt of antipyrylaminodiacetic acid, however, is pale blue, pointing to absence of affinity in the tertiary-bound nitrogen atoms.

There can, therefore, be little doubt that the molecular complexes of what are substantially the same series of neutral salts with antipyrylaminodiacetic acid have their origin in the residual affinity of the carbonyl group.

Experimental.

Salts of Antipyrylaminodiacetic Acid.

The *calcium* salt is prepared by boiling the concentrated solution of the calcium chloride compound of the free acid (*vide infra*) with excess of calcium carbonate and filtering while still hot, when it quickly sets to a mass of minute prisms sparingly soluble in cold water, but more readily on warming. It forms at least two hydrates, containing, respectively, 12 and 6 molecules of water of crystallisation, the lower hydrate being obtained by rapid crystallisation from warm solution (Found in *dodecahydrate*, Ca = 6·9; loss in a vacuum over H_2SO_4 = 37·4. $C_{15}H_{15}O_5N_3Ca,12H_2O$ requires Ca = 7·0; H_2O = 37·7 per cent. Found in *hexahydrate*, Ca = 8·7; loss in a vacuum over H_2SO_4 = 23·2; Ca in dried salt = 10·9, 11·0. $C_{15}H_{15}O_5N_3Ca,6H_2O$ requires Ca = 8·6; H_2O = 23·2 per cent. $C_{15}H_{15}O_5N_3Ca$ requires Ca = 11·2 per cent.).

The *barium* salt is obtained by heating a concentrated aqueous solution of the barium chloride addition compound (*vide infra*). It separates rapidly on stirring in minute, flattened prisms containing one and a-half molecules of water of crystallisation. The ammonium salt, obtained from the calcium salt by addition of excess of ammonium oxalate in boiling solution, yields the same product. It is, however, very difficult to remove the last traces of calcium oxalate, which are held in solution with great persistency. The barium salt is soluble in cold water, and separates on heating the solution on the water-bath in well-formed, rectangular plates. It thus shows the properties of the barium glycerylphosphates, but crystallises much more handsomely (Found, for different preparations: H_2O = 5·2, 5·7; Ba in anhydrous salt = 30·2, 29·7.

$C_{15}H_{15}O_5N_3Ba,1\frac{1}{2}H_2O$

requires H_2O = 5·6. $C_{15}H_{15}O_5N_3Ba$ requires Ba = 30·2 per cent.).

The *strontium* salt was prepared from the calcium salt *via* the ammonium salt. It crystallised, like the calcium salt, in clusters of needles containing either 9 or 6 molecules of water of crystallisation (Found for *nonahydrate*: Sr = 15·4, 15·5.

$$C_{15}H_{15}O_5N_3Sr,9H_2O$$

requires Sr = 15·45 per cent. Found for *hexahydrate*: H_2O = 21·5; Sr in anhydrous salt = 21·4. $C_{15}H_{15}O_5N_3Sr,6H_2O$ requires H_2O = 21·1. $C_{15}H_{15}O_5N_3Sr$ requires Sr = 21·6 per cent.).

The *sodium* and *potassium* salts were also obtained crystalline. They are much more readily soluble in water than the salts already described, but separate in well-defined prisms from very concentrated solutions. The *copper* salt forms a pale blue, crystalline powder, somewhat sparingly soluble in cold water.

Additive Compounds of Antipyrylaminodiacetic Acid with Neutral Salts.

With Calcium Chloride.—To a solution of 4·73 grams of chloroacetic acid in 12·5 c.c. of water were added 8 grams of calcium carbonate and 5·1 grams of 4-aminoantipyrine. The mixture was heated to boiling for two hours, a further 1·2 grams of chloroacetic acid and 2·6 grams of calcium carbonate added, and the heating continned for a further two hours. After filtration, the solution was concentrated somewhat and acidified with hydrochloric acid (Congo paper), when, on keeping, it set to a mass of crystals, which were purified by recrystallisation from water. The compound forms well-defined, rhombic prisms, which, on heating, effervesce at 165° (corr.). It dissolves readily in water or alcohol, hut sparingly, if at all, in benzene, chloroform, ether, or light petroleum. Addition of sodium chloride to the concentrated aqueous solution causes deposition of the free acid as an oil. It usually contains 8 molecules of water of crystallisation, but two other hydrates have been obtained containing 5 and 4 molecules of water respectively. The pentahydrate only loses 3 molecules of water at 60° in a vacuum. The tetrahydrate separates in large, hard crystals (Found, in *octahydrate*: Cl = 8·0, 8·1; N = 9·5, 9·6; Ca = 4·4. M.W. by titration with baryta = 891·3. Loss in a vacuum over H_2SO_4 = 15·43. $(C_{15}H_{17}O_5N_3)_2,CaCl_2,8H_2O$ requires Cl = 7·9; Ca = 4·5; N = 9·4; H_2O = 16·13 per cent. M.W. = 893·6).

(Found, in *pentahydrate*, loss in a vacuum over H_2SO_4 = 10·5; loss at 60° in a vacuum = 6·2; Cl = 8·4. M.W. by titration = 846·6. $(C_{15}H_{17}O_5N_3)_2,CaCl_2,5H_2O$ requires H_2O = 10·7; Cl = 8·4; loss of $3H_2O$ = 6·4 per cent. M.W. = 839·6.)

(Found, in *tetrahydrate*, M.W. by titration = 818·0; loss in a vacuum = 8·9. Calc.: H_2O = 8·8 per cent. M.W. = 821·5.)

With Calcium Bromide.—This complex was prepared by faintly acidifying (Congo paper) a concentrated solution or a suspension of the calcium salt, when it crystallised readily in well-defined prisms containing 11 molecules of water of crystallisation (Found: M.W. by titration = 1037. Calc.: M.W. = 1036·6).

A second hydrate was obtained crystallising in tufts of soft, silky needles. It contained 6½ molecules of water of crystallisation (Found: M.W. by titration = 956; Br = 16·8; H_2O = 12·4; Ca = 4·3. $(C_{15}H_{17}O_5N_3)_2,CaBr_2,6\frac{1}{2}H_2O$ requires Br = 16·7; H_2O = 12·3; Ca = 4·2 per cent. M.W. = 955·5).

With calcium iodide, the product was not homogeneous, the calcium : iodine ratio being approximately 1 : 1·5, and the proportion of iodine decreasing on recrystallisation. The ratio was not altered appreciably by the addition of various proportions of calcium iodide to the solution before rendering neutral or faintly acid to Congo paper.

With Strontium Chloride.—The addition product of the acid and strontium chloride is decomposed by water, with liberation of the free acid as an oil. The pure crystalline complex is obtained in the form of small needles by keeping a concentrated solution of strontium antipyrylaminodiacetate to which concentrated hydrochloric acid has been added until there is incipient formation of an oil, at 0°, for some hours. It contains 2½ molecules of water of crystallisation (Found: M.W. by titration = 840; H_2O = 5·7; Cl = 8·4. $(C_{15}H_{17}O_5N_3)_2,SrCl_2,2\frac{1}{2}H_2O$ requires H_2O = 5·3; Cl = 8·4 per cent. M.W. = 842).

With Sodium Chloride.—The double compound with sodium chloride is obtained by acidification of the concentrated solution of the sodium salt with hydrochloric acid. It forms a felted mass of minute, prismatic needles readily soluble in water or in alcohol and containing 3 molecules of water of crystallisation (Found: Cl = 8·2; N = 9·9; Na = 5·2. $C_{15}H_{17}O_5N_3,NaCl,3H_2O$ requires Cl = 8·2; N = 9·7; Na = 5·3 per cent.).

With Potassium Chloride.—This is prepared in a manner similar to that described above. It separates in clusters of small, needle-shaped prisms containing $3H_2O$ (Found: Cl = 7·8; N = 9·5; K = 8·6. $C_{15}H_{17}O_5N_3,KCl,3H_2O$ requires Cl = 7·9; N = 9·4; K = 8·7 per cent.).

With Lithium Chloride.—This derivative crystallises in minute, rhombic prisms containing $3H_2O$ (Found: Cl = 8·4.

$$C_{15}H_{17}O_5N_3,LiCl,3H_2O$$

requires Cl = 8·5 per cent.).

Additive Compounds of the Salts of Antipyrylaminodiacetic Acid with Neutral Salts.

The *calcium chloride* compound of the calcium salt remains in the residual liquor from the preparation of the calcium salt from the calcium chloride compound of the acid. It forms minute, hair-like needles, which contain 12 molecules of water of crystallisation. Unlike the barium chloride compound of the barium salt, it does not dissociate in solution with separation of the calcium salt on heating or on seeding with the salt (Found: Ca=11·4; Cl=6·7. $(C_{15}H_{15}O_5N_3Ca)_2,CaCl_2,12H_2O$ requires Ca=11·5; Cl=6·8 per cent.).

The *barium chloride* compound of the barium salt was prepared by the interaction of aminoantipyrine and chloroacetic acid in presence of barium carbonate, and separated before acidification as a mass of minute, silky needles containing 12 molecules of water of crystallisation. It dissociated on heating in aqueous solution, with formation of the free barium salt (Found: Ba=30·9; Cl=5·4; H_2O=16·5. $(C_{15}H_{15}O_5N_3Ba)_2,BaCl_2,12H_2O$ requires Ba=30·9; Cl=5·4; H_2O=16·2 per cent.).

The *magnesium chloride* compound of the magnesium salt was prepared in the same manner, using magnesia in place of barium carbonate. It dissolved fairly readily in water, from which it separated in diamond-shaped plates containing 11 molecules of water of crystallisation (Found: Mg=7·4, H_2O=20·3. $(C_{15}H_{15}O_5N_3Mg)_2,MgCl_2,11H_2O$ requires Mg=7·5; H_2O=20·3 per cent. Found, in dried material: Cl=9·1. Calc.: Cl=9·1 per cent.).

The *strontium chloride* compound of the strontium salt was prepared by crystallising the salt in presence of a considerable excess of strontium chloride. When one, two, or three molecular proportions of the chloride were present, only the strontium salt separated. It crystallised in well-defined, flattened prisms containing $11H_2O$ (Found: Sr=22·7; Cl=6·3; H_2O=17·4.

$$(C_{15}H_{15}O_5N_3Sr)_2,SrCl_2,11H_2O$$

requires Sr=22·6; Cl=6·1; H_2O=17·0 per cent.).

Antipyrylaminodiacetic Acid and its Ethyl Ester.

Antipyrylaminodiacetic acid could not be obtained crystalline, in spite of many attempts. It forms a colourless, viscid syrup readily soluble in water or in alcohol. The *ethyl* ester, prepared by esterification with alcoholic hydrogen chloride or hydrogen sulphate, was obtained after removal of most of the alcohol, addi-

tion of water, basification with sodium carbonate, saturation with sodium chloride, and extraction with ether, as a pale yellow oil, which did not crystallise after remaining for several months over paraffin wax in a desiccator. On distillation at 10 mm. pressure, it decomposed completely. Before analysis, it was left for a considerable time in a partial vacuum over potassium hydroxide, calcium chloride, and paraffin wax (Found: C=61·2; H=7·0; N=10·9. $C_{19}H_{25}O_5N_3$ requires C=60·8; H=6·7; N=11·2 per cent.).

WELLCOME CHEMICAL RESEARCH LABORATORIES.
[Received, January 26th, 1921.]

XXXIX.—*An Investigation on the Influence of Negative Groups of Different Character on the Reactivity of Hydrogen Atoms Carried by the Same Carbon Atom. Part I.*

By BIRAJ MOHAN GUPTA.

THIS investigation was undertaken with a view to obtain a clearer insight into the mechanism of the reactivity of the methylene group in compounds of the type CH_2RR', where either one or both of the radicles are so-called negative groups, and also to obtain, if possible, a quantitative idea of the influence exerted individually by such groups.

The points on which elucidation is ultimately aimed at may be enumerated as below:

(*a*) The exact conditions which control the reactivity of the methylene group with respect to a particular reagent, for example, an aldehyde.

(*b*) The connexion between the reactivity and the displacement of an atom of hydrogen by a metal or the ionising capacity of this group.

(*c*) The connexion between this reactivity and the negative character of the adjacent radicle.

(*d*) Whether this reactivity, as well as the negative character of the radicle, is really the effect of the unsaturated character of the adjacent multivalent elements.

(*e*) How far this reactivity is connected with the phenomenon of tautomerism.

Of the numerous, commonly accepted negative groups, if only six, such as the cyanogen, carbethoxy-, acetyl, carbamyl, *p*-nitrophenyl, and phenyl radicles, are selected, twenty-one compounds in all fall within the purview of the comparative study.

The action of aldehydes on a large number of these compounds has been studied more or less exhaustively by many investigators. An analysis of the methods employed, the experimental conditions observed, and the yields obtained in the interaction of these substances with two typical aldehydes, such as acetaldehyde and benzaldehyde, reveals the following regularity.

There is no appreciable action when these substances are simply treated with aldehydes. In scarcely any case does condensation take place on direct heating. Combination takes place when the mixture is treated with a few drops or a larger quantity of ammonia, diethylamine, piperidine, a dilute solution of potassium cyanide, dilute or concentrated solutions of sodium or potassium hydroxide, sodium ethoxide, concentrated hydrochloric acid, or with a stream of dry hydrogen chloride gas.

In the present communication the results are recorded of the action of some aldehydes on compounds of the type

$$R\cdot CH_2\cdot CO\cdot NH_2,$$

where R is the phenyl, *p*-nitrophenyl, or carbethoxy-group.

The action of aldehydes on cyanoacetamide has been studied by Heuck (*Ber.*, 1895, **28**, 2251), and more recently by Thorpe and Day (T., 1920, **117**, 1465). They found that combination usually takes place at the methylene group. By the action of benzaldehyde on malonamide, Heuck (*loc. cit.*) obtained a compound, for which the formula $CHPh{:}C(CO\cdot NH_2)_2$ has been established. By the interaction of benzaldehyde and diethylmalonamide, however, Burrows and Keane (T., 1907, **91**, 269) obtained the substance, $CEt_2{<}{CO\cdot NH \atop CO\cdot NH}{>}CHPh$. This shows that in malonamide the hydrogen atoms of the methylene group are more reactive to aldehydes than the hydrogen atoms of the carbamyl groups.

In the case of phenylacetamide, however, contrary to expectation, it has been found that the reaction takes place at the amido-group instead of at the methylene group. The result is all the more surprising in view of the fact that phenylacetonitrile and ethyl phenylacetate react with aldehydes at the methylene group (Frost, *Annalen*, 1889, **250**, 156—166; Oglialoro, *Gazzetta*, 1878, **8**, 429).

When the phenyl group is substituted by the carbethoxy-group, it has been found that acetaldehyde attacks the methylene group,

producing ethyl α-carbamylcrotonate, CHMe:C(CO_2Et)·CO·NH_2, or ethyl αα'-dicarbamyl-β-methylglutarate,

CHMe[CH(CO·NH_2)·CO_2Et]$_2$,

according to the proportion of ethyl malonamate used. When, on the other hand, the nitrophenyl group is substituted for the phenyl group, the point of attack by the aldehyde cannot be shifted from the amido-group to the methylene group.

These experiments indicate that the reactivity of the methylene group depends on the total negative character of both radicles, and that if this does not reach a certain limit, the reactivity of the methylene group vanishes, at least with respect to aldehydes.

EXPERIMENTAL.

A. *Phenylacetamide.*

This substance was prepared by the action of concentrated sulphuric acid on phenylacetonitrile, according to the method described by Purgotti (*Gazzetta*, 1890, **20**, 178). After crystallisation from hot water, the substance melted at 154·5°.

Action of Acetaldehyde.

Ethylidenebisphenylacetamide is immediately formed when a mixture of phenylacetamide and acetaldehyde is treated with a few drops of concentrated hydrochloric acid. The fact that reaction takes place at the amido-group is proved by the conversion of the substance into acetaldehyde and phenylacetic acid on boiling with dilute hydrochloric acid (Bernthsen, *Annalen*, 1877, **184**, 318). With the object of attacking the methylene group, phenylacetamide was treated with the equivalent quantity of acetaldehyde and a few drops of various catalysts, such as diethylamine, dilute ammonia, sodium hydroxide, sodium ethoxide, or a 50 per cent. aqueous solution of potassium hydroxide. No reaction took place, even when the experimental conditions were varied by increasing the quantity of acetaldehyde and by carrying out the operation in aqueous or alcoholic solution, either at the ordinary temperature or at 0°.

Action of Benzaldehyde.

Benzylidenebisphenylacetamide, CHPh(NH·CO·CH_2Ph)$_2$.—A mixture of phenylacetamide (13·4 grams) and benzaldehyde (5·3 grams) was heated at about 160° during about two hours. The solid mass obtained on cooling was finely powdered and washed with hot

alcohol, and the product (yield about 75 per cent.) crystallised from hot alcohol, from which it separated in fine needles melting at 225° (Found, C=76·6; H=6·13; N=8·05. $C_{23}H_{22}O_2N_2$ requires C=77·03; H=6·20; N=7·83 per cent.).

In order to determine its constitution, and more particularly to ascertain whether the reaction took place at the methylene or at the amido-group, the condensation product was boiled with an alcoholic solution of potassium hydroxide, whereby benzaldehyde and ammonia were evolved. After removing the remaining benzaldehyde in a current of steam, the contents of the flask were concentrated and faintly acidified with dilute hydrochloric acid, the slight amount of resinous matter filtered off, and the clear filtrate again concentrated. On cooling, crystals of phenylacetic acid melting at 77° were obtained.

One gram of the compound was heated with 5 c.c. of concentrated hydrochloric acid in a sealed tube for six hours at 125°. On opening the tube the odour of benzaldehyde was perceptible and a white precipitate was gradually deposited. After filtering off resinous matter and evaporating the filtrate, crystals of phenylacetic acid were obtained.

These experiments indicate that in this compound the aldehydic residue is linked at the amido-group, and not at the methylene group.

Action of Anisaldehyde.

Anisylidenebisphenylacetamide, $MeO{\cdot}C_6H_4{\cdot}CH(NH{\cdot}CO{\cdot}CH_2Ph)_2$. —A mixture of anisaldehyde (6·8 grams) and phenylacetamide (13·5 grams) was heated at 160—170° for about two hours. The solid mass obtained on cooling was finely ground with hot alcohol and washed with alcohol to remove the unchanged aldehyde. The substance dissolved very slightly in cold alcohol, but fairly well in hot alcohol, from which it crystallised in very light, fine needles melting at 241° (Found, C=73·99; H=6·27; N=7·04. $C_{24}H_{24}O_3N_2$ requires C=74·18; H=6·24; N=7·23 per cent.).

Action of Cinnamaldehyde.

Cinnamylidenebisphenylacetamide,

$$CHPh{:}CH{\cdot}CH(NH{\cdot}CO{\cdot}CH_2Ph)_2.$$

—A mixture of cinnamaldehyde (6·2 grams) and phenylacetamide (13·5 grams) was heated at 160—170° for about two hours, and the product treated as described above. It was insoluble in water, but soluble in hot alcohol, from which it was crystallised. It melted at

238° (Found, C=77·91; H=6·46; N=7·45. $C_{25}H_{24}O_2N_2$ requires C=78·07; H=6·31; N=7·30 per cent.).

Action of Phenylacetaldehyde.

Phenylethylidenebisphenylacetamide,

$CH_2Ph·CH(NH·CO·CH_2Ph)_2$,

was obtained from phenylacetamide (13·7 grams) and phenylacetaldehyde (6 grams) in the manner described above. It was insoluble in water, but soluble in hot alcohol or benzene. It did not crystallise well from alcohol, but silky needles, m. p. 223°, were obtained from the solution in benzene (Found, C=76·9; H=6·5; N=7·80. $C_{24}H_{24}O_2N_2$ requires C=77·3; H=6·5; N=7·54 per cent.).

B. p-*Nitrophenylacetamide.*

This substance was prepared by gradually adding 20 grams of phenylacetamide to a well-cooled mixture of 20 grams of concentrated nitric acid and 40 grams of concentrated sulphuric acid, according to the method described by Purgotti (*Gazzetta*, 1890, **20**, 593). After crystallisation from hot alcohol it melted at 191°.

Action of Acetaldehyde.

Ethylidenebis-p-*nitrophenylacetamide,*

$CHMe(NH·CO·CH_2·C_6H_4·NO_2)_2$.

—This substance was obtained by treating a mixture containing 3·6 grams of *p*-nitrophenylacetamide and 3 grams of acetaldehyde with 2 drops of concentrated hydrochloric acid. A vigorous reaction took place, and a large amount of heat was evolved. The product was washed first with water and then with a little alcohol. The yield was about 85 per cent. The substance is insoluble in water, but is sparingly soluble in hot alcohol. After crystallisation from the latter solvent it melts at 250° (Found, C=55·28; H=4·80; N=14·4. $C_{18}H_{18}O_6N_4$ requires C=55·09; H=4·70; N=14·5 per cent.).

One gram of the condensation product was boiled with 15 c.c. of dilute hydrochloric acid (1:2) for two hours. It dissolved completely, and after filtering off the slight amount of resinous matter formed, the clear filtrate deposited needle-shaped, colourless crystals, which melted at 151° and proved to be *p*-nitrophenylacetic acid.

The reactivity of the amido-group of *p*-nitrophenylacetamide with acetaldehyde under the influence of hydrochloric acid is completely inhibited in aqueous solution. In this respect *p*-nitrophenylacet-

amide differs from phenylacetamide, in which case at least a partial reaction takes place.

With the object of attacking the methylene group of *p*-nitrophenylacetamide, mixtures of this substance with acetaldehyde were treated with a few drops of diethylamine or a 50 per cent. solution of potassium hydroxide in water. In these cases *p*-nitrophenylacetamide did not react at all.

C. *Ethyl Malonamate.*

This compound was prepared by Pinner's method (*Ber.*, 1895, **28**, 479). A mixture of ethyl cyanoacetate (45·2 grams) and absolute alcohol (18·4 grams) was well cooled in a freezing mixture, while a very slow stream of dry hydrogen chloride gas was passed in during about twelve hours until there was an increase in weight of 14·4 grams. On keeping overnight, almost the whole of the mixture solidified, a white, crystalline mass of the imino-ether hydrochloride, $CO_2Et{\cdot}CH_2{\cdot}C(OEt){:}NH,HCl$, being produced. After pouring off the liquid, the flask was heated on a water-bath for two to three hours until acid and irritating vapours ceased to be evolved. The molten contents were filtered, heated again on the water-bath to ensure complete separation of ammonium chloride, filtered once more, and cooled in ice, when needle-shaped crystals of ethyl malonamate were deposited. After having been washed with a little dry ether and dried on a porous plate, the product melted at 50°. The yield was about 50 per cent. of the theoretical.

Action of Acetaldehyde.

Ethyl a-Carbamylcrotonate, $CHMe{:}C(CO_2Et){\cdot}CO{\cdot}NH_2$.—A mixture of 13·1 grams of ethyl malonamate with 4·4 grams of freshly distilled acetaldehyde became homogeneous after the addition of two drops of diethylamine, a slight amount of heat being evolved. The liquid was cooled overnight in a freezing mixture, when almost the whole of it solidified. The viscous mother liquor was removed by porous plate, and the white, crystalline powder washed with dry ether. It melted at 78° (Found, C=52·8; H=7·0; N=9·2. $C_7H_{11}O_3N$ requires C=53·47; H=7·06; N=8·93 per cent.). The product, obtained in a yield of about 80 per cent., was very soluble in water and in alcohol.

This substance has a tendency to react additively with ethyl malonamate (1 mol.) in the presence of a little alcohol or water to form ethyl *aa'*-dicarbamyl-*β*-methylglutarate.

Ethyl αα′-Dicarbamyl-β-methylglutarate, $CHMe[CH(CO{\cdot}NH_2){\cdot}CO_2Et]_2$.—13·1 Grams of ethyl malonamate were treated with 2·2 grams of freshly distilled acetaldehyde. The mixture was brought to a clear solution by the addition of 3 c.c. of water, treated with 4 drops of a 50 per cent. aqueous solution of potassium hydroxide, and cooled in ice-water. Small, granular crystals, which began to be deposited after two or three hours, were separated after twenty-four hours. The yield was about 73 per cent. of the theoretical. The crude product was washed quickly with water and crystallised from hot alcohol, when white, granular crystals melting at 177·5° were obtained (Found, C=49·99; H=7·14; N=10·07. $C_{12}H_{20}O_6N_2$ requires C=49·96; H=6·99; N=9·73 per cent.).

This substance could not be prepared in alcoholic solution with diethylamine as catalyst, but was easily formed when a mixture containing ethyl malonamate, acetaldehyde, and several drops of diethylamine was seeded with a few crystals of the condensed product.

One gram of ethyl αα′-dicarbamyl-β-methylglutarate was warmed with 2·5 c.c. of concentrated hydrochloric acid, and the clear solution boiled for two hours under reflux, after having been diluted with an equal volume of water. The solution was cooled and extracted with ether. The residue obtained after removing the solvent melted at 74—82°. It was dissolved in the least possible quantity of water and the solution saturated with dry hydrogen chloride. On cooling, it deposited crystals of β-methylglutaric acid, m. p. 87° (compare Knoevenagel, *Ber.*, 1898, **31**, 2585).

The author wishes to record his best thanks to Professor J. F. Thorpe for his suggestions and his kind interest in the progress of this work, and to acknowledge that a grant from the Research Fund of the Chemical Society was used to defray part of the expense incurred in this investigation.

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, S.W.

[*Received, December 22nd*, 1920.]

XL.—*The Conditions Underlying the Formation of Unsaturated and of Cyclic Compounds from Halogenated Open-chain Derivatives. Part I. Products Derived from α-Halogenated Glutaric Acids.*

By Christopher Kelk Ingold.

In the series of papers of which this is Part I, it is proposed to examine the reason for the failure of Baeyer's strain theory to account satisfactorily for the relative ease of formation and the stability of the different types of carbon ring.

An illuminating example of the difficulties experienced in attempting to apply Baeyer's theory to the simple homocyclic rings is furnished by the experiments of Stohmann and Kleber (*J. pr. Chem.*, 1892, [ii], **45**, 475) on their heats of formation. These investigators found that the quantities of heat absorbed in the formation of similarly constituted compounds containing the *cyclo*propane, *cyclo*butane, *cyclo*pentane, and *cyclo*hexane rings by the removal of two atoms of hydrogen from corresponding open-chain substances were as follows:

Ring	*cyclo*-Propane.	*cyclo*-Butane.	*cyclo*-Pentane.	*cyclo*-Hexane.
Angle of strain (Baeyer) ...	24·7°	9·7°	0·7°	5·3°
Heat absorbed (S. and K.) ...	38·1	42·6	16·1	14·3 cals.

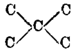
For the sake of comparison, the angles which Baeyer regards as indicating the relative instability of the different ring systems are tabulated with the figures for the heat absorbed in ring formation. The discordance is most pronounced. If the thermal numbers are used to construct a "curve of instability," *cyclo*butane occupies a position at the crest of the curve; according to theory, *cyclo*propane should be situated at the highest point. Again, *cyclo*hexane takes the lowest position, which in theory should be occupied by *cyclo*pentane. Furthermore, the difference between the thermal figures for *cyclo*pentane and *cyclo*hexane is very trifling, whereas Baeyer's theory would lead one to expect a large difference of stability. In fact, the curves on which the two series of numbers lie belong to quite different families: one contains a crest but no trough, and the other a trough but no crest.

General experience conforms with the thermal measurements rather than with the strain theory. Thus it has repeatedly been observed that methods of preparation of five-, six-, and even three-carbon rings fail, either wholly or partly, when applied to the

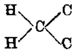
production of *cyclo*butane rings. With regard to five- and six-membered rings, there is on record a wealth of data indicating that they have practically equal stability, a fact which, although in accord with the thermochemical results, is in serious conflict with theory.

In the face of such difficulties in the examination by means of Baeyer's theory of the simplest types of ring, it is obviously impossible to expect that an indiscriminate application of the theory to more complex cases, such as those afforded by the *spiro*- and associated ring compounds now under investigation in these laboratories, will prove of service in elucidating molecular condition; it is therefore necessary to re-examine the question in a more fundamental manner.

The tetrahedral angle of Baeyer ($2 \tan^{-1} \sqrt{2} = 109 \cdot 5^{\circ}$) is the angle at the centre of a regular tetrahedron subtended by one of its sides. It is probable, however, that the tetrahedron representing a carbon atom is approximately regular only when the carbon atom is attached to four atoms of a similar kind, for example, to four carbon atoms (*A*). The basic unit of all the polymethylene rings is, however, not quaternary carhon, but secondary carbon (*B*). Now, as Kopp, Traube, and others have shown, the hydrogen



(*A*.)



(*B*.)

atom in organic compounds occupies a much smaller volume than the carbon atom, and it is therefore possible that in the methylene group (*B*) the two carbon atoms attached to the central one occupy more of tbe surrounding space than do the two hydrogen atoms. If this is so, the angle between the carbon-to-carbon valencies of a polymethylene chain will not be $109 \cdot 5^{\circ}$, as hitherto supposed, but will be some angle greater than this.

It may be stated at once that this inference is strongly supported by the experiments of this series so far as they have as yet progressed, as well as by a considerable body of evidence from other quarters.

To each of the four atoms attached to the central carbon atom of the methylene group (*B*) may be allocated a spherical domain the cubic content of which, according to the hypothesis adopted, is proportional to the atomic volume of the element. Apart from this condition, the size assumed for these domains is immaterial, and, indeed, they need not even be regarded of necessity as mutually exclusive. If, however, the centres are first fixed by supposing the spheres to be in mutual contact, and are then joined to

one another and to the centre of an internal sphere having contact with the other four, there is obtained an irregular tetrahedron with two planes of symmetry. If V and v are the atomic volumes of carbon and hydrogen, respectively, the longest edge of this tetrahedron will be proportional to $V^{\frac{1}{3}}$, and the angle 2θ subtending it at the internal point will be the required angle between the carbon-to-carbon valencies. Similarly, the shortest edge will be proportional to $v^{\frac{1}{3}}$, and the subtending angle, 2ϕ, the angle between the valencies attaching hydrogen.

It is not difficult to show that in these circumstances θ and ϕ are given by the equations

$$V^{\frac{1}{3}}\sin\phi - v^{\frac{1}{3}}\sin\theta = (V^{\frac{1}{3}} - v^{\frac{1}{3}})\sin\theta\sin\phi$$

and

$$V^{\frac{1}{3}}\cot\theta + v^{\frac{1}{3}}\cot\phi = \sqrt{2}(Vv)^{\frac{1}{6}},$$

of which the solution for θ is

$$\operatorname{cosec}\theta = 1 + v^{\frac{1}{3}}.\frac{\sqrt{6}(Vv)^{\frac{1}{6}} - (V^{\frac{1}{3}} + v^{\frac{1}{3}})}{2(Vv)^{\frac{1}{6}} - (V^{\frac{1}{3}} - v^{\frac{1}{3}})}.$$

Using Traube's values (*Ahrens' Vorträge*, 1899, **4**, 255) for V and v, we have, finally, $2\theta = 115{\cdot}3°$; that is to say, the angle between each pair of carbon-to-carbon valencies in a polymethylene chain is nearly 6° greater than has hitherto been commonly supposed.

Accepting the new value, it is possible to calculate by how much the terminal carbon atoms of a *n*-propane chain must approach one another in forming a *cyclo*propane ring, those of a *n*-butane chain in forming a *cyclo*butane ring, and so on. The figures thus obtained, namely:

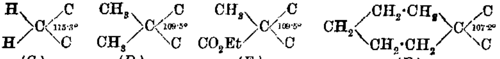
*cyclo*Propane.	*cyclo*Butane.	*cyclo*Pentane.	*cyclo*Hexane.	*cyclo*Heptane.
0·345	0·427	0·220	0·207	0·730

are not only in excellent functional agreement with the thermal determinations of Stohmann and Kleber, but are also in complete qualitative accord with more purely chemical experience of the formation of such rings, in particular, with the difficulty with which the closure of the four-carbon ring is attended, and with the almost equal ease of formation of five- and six-membered carbon rings.

The striking effect, of which hitherto no explanation appears to have been suggested, of the *gem*-grouping in promoting ring formation, is also very easily accounted for. Besides the numerous examples of this phenomenon occurring in the chemistry of the camphors and the bicyclic terpenes, there are many which have been furnished by synthetical experiments, particularly in con-

nexion with the preparation of *gem*-dimethyl*cyclo*propane and *gem*-dimethyl*cyclo*pentane compounds.* Thus Perkin and Thorpe found that αα-dimethylbutane-αβδ-tricarboxylic acid was smoothly converted into a *cyclo*pentanone derivative merely on boiling its sodium salt with acetic anhydride (T., 1904, **85**, 138), a change which has never been observed to occur with adipic acids containing no *gem*-dialkyl grouping. The effect is equally apparent in heterocyclic ring formation. Thus, whilst the α-hydroxy- and the αα′-dihydroxy-derivatives of ββ-dimethylglutaric acid cannot be obtained in the free state, owing to their tendency to change into lactones, the corresponding hydroxy- and dihydroxy-glutaric acids can readily be isolated, and are comparatively stable substances (pp. 321, 322, and 323). Similarly, whilst glutaric anhydride is easily decomposed by water, ββ-dimethylglutaric anhydride may be boiled for hours with but little change, and αββ-trimethylglutaric anhydride actually crystallises from hot water with water of crystallisation (Perkin and Thorpe, T., 1899, **75**, 65). It may also be noted that the only known β-lactones contain the *gem*-dialkyl grouping (Baeyer and Villiger, *Ber.*, 1897, **30**, 1955).

These contrasts are clearly explicable by the theory that groups attached to a carbon atom bearing two methyl radicles, for example (*D*), are in closer proximity than the same, or similar, groups attached to a carbon atom combined with two hydrogen atoms (*C*).



(*C*.) (*D*.) (*E*.) (*F*.)

Probably the comparatively considerable stability of dialkyl- and diaryl-ketens is to be ascribed to the same cause.

The fact that these effects are not due to the repulsion of electrically similar methyl groups, but are essentially connected with volume relations, is proved by the occurrence of cases in which such electrically dissimilar groups as methyl and carbethoxyl take the place (*E*) of the *gem*-dialkyl grouping, such as, for example, that of methyldiacetylsuccinic ester, which, under exceedingly mild conditions, is converted into a five-carbon ring ketone, a type of change which cannot be brought about in the case of the unmethylated analogue (Willstätter and Clarke, *Ber.*, 1914, **47**, 298).

* Mr. Kon of this laboratory has in progress some interesting experiments illustrating the same point in relation to *cyclo*butane derivatives.

When the components of the *gem*-grouping themselves form part of a ring (*F*), a further convergence of the attached groups may take place (Beasley, Ingold, and Thorpe, T., 1915, **107**, 1080).

In direct contrast to the effect of the *gem*-grouping in promoting the closure * of three-, four-, and five-membered carbon rings is that of the semi-cyclic double bond. Clearly, according to the hypothesis that the spatial configuration of unstrained molecules is determined by the relative volumes of the component parts, the presence of a potential semi-cyclic double bond, whilst hindering the formation of the smaller rings, should promote that of seven- and eight-carbon rings. An instance showing that this is so is afforded by the cyclic ketones; for although *cyclo*propanone and *cyclo*butanone cannot be obtained by the Wislicenus method, *cyclo*heptanone is produced in fairly good yield.

In view of the large number of facts satisfactorily collated by the modified strain theory, it seemed desirable to undertake a series of experiments with the definite object of justifying (or otherwise) the introduction of atomic volumes into this branch of stereochemistry. The prime necessity clearly is to follow some one method of ring formation throughout all the obtainable types of alicyclic ring, starting with the *cyclo*propane ring, this being the reference case with which the closure of other rings is to be compared. Furthermore, it is necessary that the method of experiment should be carefully standardised, and, so far as possible, placed on a quantitative basis.

Much depends on the method of ring formation adopted. It is clearly unsatisfactory to employ a method such as that of Dieckmann, which fails in its application to the lower rings through the entrance into the reaction of more than one molecule of the open-chain substance. Again, Perkin's method, although widely applicable, suffers from the disadvantage that the results are affected by the reversible alcoholysis of the sodio-esters employed, and it is difficult, therefore, to draw conclusions regarding the questions now at issue. Further, it is evident that, although the reaction chosen must be of a sufficiently enforced character to

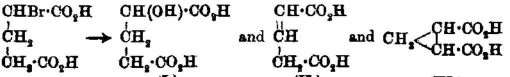
* It is proposed to deal in this paper only with the formation of rings and not with their stability. The latter also is very dependent on the attached groups, and is conditioned in particular by the curvature of the most curved valency in the molecule (Ingold and Thorpe, T., 1919, **115**, 320). The maximal curvatures for the unsubstituted polymethylene hydrocarbons calculated from $2\theta = 115{\cdot}3^{\circ}$ are as follows, there being *no* maximum at *cyclo*butane:

*cyclo*Propane.	*cyclo*Butane.	*cyclo*Pentane.	*cyclo*Hexane.	*cyclo*Heptane
0·927	0·436	0·126	0·084	0·230

ensure the production, at least to some extent, of the more highly strained rings, there should always be possible under the conditions of the experiments some standard side-reaction with which ring formation may compete. The progress of ring formation in competition with the side-reaction is, then, a measure of the ease of production of the ring.

The reaction which appeared best to fulfil these conditions was that by which caronic acid was first prepared (Perkin and Thorpe, T., 1899, **75**, 48) from ββ-dimethylglutaric acid, namely, the elimination of hydrogen bromide by means of alkali from the α-bromo-substitution product. The method has since been applied to the production of cyclic compounds from other ββ-disubstituted glutaric acids (T., 1915, **107**, 1080; 1920, **117**, 591, 1579). In all these cases, the formation of an unsaturated derivative simply by the elimination of hydrogen bromide from the bromo-acid is impossible; very little work appears to have been done on the application of the method to the more simply constituted dibasic acids, such as glutaric and adipic acids, the α-halogen derivatives of which might be expected to yield unsaturated as well as cyclic elimination products.

The standard side-reaction in all these cases is the replacement of the halogen atom by the hydroxyl group, a reaction which, so far as has been ascertained by preliminary experiments, takes place with approximately equal ease when the different bromo-acids are treated with dilute solutions of alkalis. Under these conditions, the extent to which direct elimination of hydrogen bromide occurs is always slight, even if capable of detection. When, however, more concentrated solutions of the alkali are used, and particularly when water is replaced by alcohol as solvent, direct elimination is favoured at the expense of hydroxylation, and may become the principal reaction. The elimination may, moreover, proceed in two directions, to give in the one case an unsaturated acid and in the other a cyclic compound. Thus from every monobromo-dibasic acid there should arise three products. α-Bromoglutaric acid should yield α-hydroxyglutaric acid (I), glutaconic acid (II), and *cyclo*propanedicarboxylic acid (III).



(I.) (II.) (III.)

Similarly, α-bromoadipic acid should give α-hydroxyadipic, Δ^{α}-dihydromuconic, and *cyclo*butanedicarboxylic acids:

$$\begin{matrix}CH_2\cdot CHBr\cdot CO_2H \\ CH_2\cdot CH_2\cdot CO_2H\end{matrix} \longrightarrow \begin{matrix}CH_2\cdot CH(OH)\cdot CO_2H \\ CH_2\cdot CH_2\cdot CO_2H\end{matrix} \text{ and}$$

$$\begin{matrix}CH{:}CH\cdot CO_2H \\ CH_2\cdot CH_2\cdot CO_2H\end{matrix} \text{ and } \begin{matrix}CH_2\cdot CH\cdot CO_2H \\ CH_2\cdot CH\cdot CO_2H\end{matrix}$$

and so on.

It was therefore to be anticipated that an examination of the proportions in which these various substances were produced from the different bromo-acids under standard experimental conditions should yield valuable evidence on the tendency to the formation of the different rings, and on the peculiar position in the theoretical scheme occupied by the double bond.

The present communication deals with glutaric acid, the *α*-mono- and *αα'*-dibromo-derivatives of which have been treated under two standard sets of experimental conditions.

It has already been shown by Perkin and Tattersall (T., 1905, **87**, 366) that *trans-cyclo*propane-1:2-dicarboxylic acid is one of the substances formed when ethyl *α*-bromoglutarate is treated with a concentrated solution of an alkali. Crystals of this acid were actually deposited from the syrup obtained by acidifying the product of the reaction. Only small quantities of material were available, however, and the nature of the syrup was not determined.

When ethyl *α*-bromoglutarate is boiled with a 2*N*-solution of sodium carbonate, simple hydroxylation occurs almost entirely, *α*-hydroxyglutaric acid (I), or its lactone, forming about 95 per cent. of the product. *trans-cyclo*Propane-1:2-dicarboxylic acid (III) is also obtained in 3 per cent. yield, but no trace of glutaconic acid (II).

With 6*N*-methyl-alcoholic potassium hydroxide as the reagent the same substances are produced, but in very different proportions, and in company with others. Glutaconic acid was isolated in this case, but only in small amount. The *cis*-form of *cyclo*propane-1:2-dicarboxylic acid was also obtained. In addition to these, a small amount of paraconic acid (IV), evidently a product of the fission

(III.) (IV.)

of one or both of the *cyclo*propanedicarboxylic acids, was isolated.

The method employed for the separation of these substances, which included a fractional distillation, rendered it impossible to

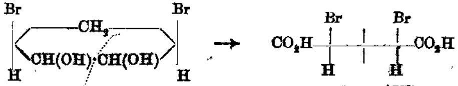
account for the whole of the material, but the products actually isolated were:

	Per cent.
a-Hydroxyglutaric acid (including its lactonic acid, which was hydrated before weighing)	16
Glutaconic acid	3
trans-*cyclo*Propane-1 : 2-dicarboxylic acid	35
cis- " " " " "	4
Paraconic acid	8
Total isolated =	66

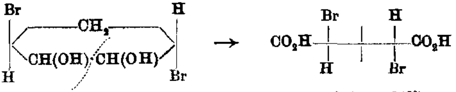
These figures indicate in an exceedingly clear manner the remarkable tendency toward the formation of *cyclo*propane derivatives by the elimination, along with bromine, of an atom of hydrogen from the *a*-carbon atom of the acid. If in place of the paraconic acid count is taken of the equivalent quantity of the *cyclo*propanedicarboxylic acid from which it must be supposed to be derived, then at least 47 per cent. of the two stereoisomeric forms of the latter acid is produced during the reaction. In striking contrast to this, the elimination of the *β*-hydrogen atom to form glutaconic acid takes place to the extent of 3 per cent. only.

It may be added that the remarkable tendency toward the formation of the *cyclo*propane ring indicated by these results is strongly brought out by the singular contrast which the investigation of mono- and dibromo-adipic acids provides. This point will be more fully examined in a further communication dealing with the behaviour of these acids.

Interesting results were obtained on extending the investigation to *aa'*-dibromoglutaric ester. The dibromination of glutaric acid has been investigated by Auwers and Bernhardi (*Ber.*, 1891, **24**, 2230), who isolated a dibromo-acid melting at 169—170°. This acid, although the least soluble and most easily isolated, is not the only product of direct dibromination, but forms about two-thirds of a mixture of two isomeric acids. These two acids, melting at 170° and 142° respectively, are evidently identical with the two bromo-acids prepared by Thiele (*Annalen*, 1901, **314**, 305) by oxidation of the *cis*- and *trans*-forms of 1 : 4-dibromo-2 : 3-dihydroxy*cyclo*pentane. Since the *cis*-form yielded only the acid of higher melting point, and the *trans*-form only the acid, m. p. 142°, it is clear that the former must be the *meso*-variety of dibromoglutaric acid and the latter the *racemic* compound:



cis. *meso* (m. p. 170°).



trans. *racemic* (m. p. 142°).

A boiling dilute solution of sodium carbonate quickly converts both these bromo-acids into the corresponding dihydroxy-acids. The product actually isolated may not be the free dihydroxy-acid, but its monolactone, or a mixture of this with the free hydroxy-acid. The dihydroxy-acid derived from the *meso*-dibromo-acid is stable up to its melting point, 162°, but above this temperature readily eliminates water, yielding a monolactonic acid, m. p. 150°. The dihydroxy-acid derived from the racemic bromo-acid is, on the contrary, much less stable. It evolves water vapour fairly rapidly at 100°, and almost instantaneously at 125°, changing into a monolactonic acid, m. p. 168°.

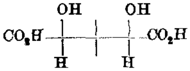
An $\alpha\alpha'$-dihydroxyglutaric acid has been prepared by Kiliani and Matthes (*Ber.*, 1907, **40**, 1238) by eliminating carbon dioxide from $\alpha\gamma$-dihydroxypropane-$\alpha\alpha\gamma$-tricarboxylic acid:

$$CO_2H\cdot CH(OH)\cdot CH_2\cdot C(OH)(CO_2H)_2 \longrightarrow$$
$$CO_2 + CO_2H\cdot CH(OH)\cdot CH_2\cdot CH(OH)\cdot CO_2H.$$

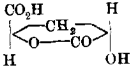
Unfortunately these investigators did not characterise the acid obtained by any derivatives other than salts, and the question of identity is therefore to some extent an open one. Kiliani and Matthes's monolactonic acid, however, melted at 168°, and a reference to their description makes it appear probable at least that their dihydroxy-acid is identical with that obtained by the action of sodium carbonate on the racemic dibromo-acid. Using an optically active tricarboxylic acid, they obtained, besides the substance here referred to, an optically active dihydroxyglutaric acid, and concluded that the inactive isomeride must therefore have the *meso*-configuration. It is clear from what has been said, however, that the substance is probably not the *meso*- but the *racemic* acid, and that it is formed by the partial racemisation of the active compound under the conditions of Kiliani and Matthes's experiment.

The new dihydroxy-acid (m. p. 162°) must therefore be regarded as the *meso*-form (V), and its hydroxy-lactone (m. p. 150°) as the *trans*-lactone (VI). The other dihydroxy-acid (decomp. below 125°) must be the racemic acid (VII), and its lactone (m. p. 168°) consequently the *cis*-lactone (VIII). The structures assigned to the lactones follow because the interconvertibility by hydration and dehydration of these with the corresponding dihydroxy-acids has

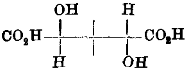
been experimentally proved. In order to avoid a recurrence of difficulties in identification the substances were characterised by



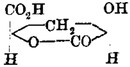
(V. m. p. 162°.)



(VI. m. p. 150°.)



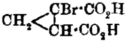
(VII. m. p. 125° dec.)



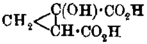
(VIII. m. p. 168°.)

means of their anilides and *p*-toluidides, which were in every way suitable for the purpose.

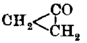
When methyl or ethyl dibromoglutarate is hydrolysed by a 2*N*-solution of sodium carbonate the above-mentioned hydroxylation products *constitute no more than about 90 per cent. of the* total yield. The remainder consists mainly of a bromo*cyclo*propanedicarboxylic acid (IX). On prolonged boiling with a solution of sodium carbonate, replacement of the bromine atom by the hydroxyl group occurs, and the *cyclo*propanoldicarboxylic acid (X) is produced:



(IX.)



(X.)



(XI.)

The action of a dilute solution of sodium carbonate on the dibromoglutaric esters therefore pursues a course closely analogous to that followed during decomposition of the monobromo-ester under the action of this reagent. Consequently, it was expected that on treating the dibromo-ester with concentrated, methyl-alcoholic potassium hydroxide the formation of hydroxylation products would be reduced to a minimum and a large yield of the hydroxy-acid (X) would result. A strong motive for endeavouring to obtain this acid in quantity was that from it, by the action of concentrated sulphuric acid, it should be possible to prepare the theoretically simplest cyclic ketone, *cyclo*propanone (XI), a supply of which is urgently required for the work on *spiro*-compounds now in progress in this laboratory. Although large quantities of the hydroxy-acid (X) were not obtained, a small amount of *cyclo*propanone, enough partly to characterise the substance, was actually prepared by this method.

The hydroxy-acid (X) cannot be obtained by the action of a con-

centrated, methyl-alcoholic solution of potassium hydroxide because the *cyclo*propane ring, although doubtless originally formed, is unstable under the conditions of the experiment. The material actually isolated consisted of hydroxylation products [(V)—(VIII)] about 10 per cent.) and a mixture of two other acids (90 per cent.). That present in smaller quantity proved to be methoxy*cyclo*propane-1 : 2-dicarboxylic acid (XII), whilst the main constituent was α-ketoglutaric acid (XIII), which has already been prepared and characterised by Blaise and Gault (*Bull. Soc. chim.*, 1911, [iv], **9**, 451) and by Wislicenus and Waldmüller (*Ber.*, 1911, **44**, 1564).

$$CH_2<\begin{matrix}C(OMe)\cdot CO_2H\\ CH\cdot CO_2H\end{matrix}\qquad\qquad CH_2<\begin{matrix}CO\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}$$

(XII.) (XIII.)

That the main bulk of the ketonic acid is produced by the fission of the *cyclo*propane ring, and not by way of a hydroxyglutaconic acid through tautomeric change:

$$CH_2<\begin{matrix}CHBr\cdot CO_2Et\\ CHBr\cdot CO_2Et\end{matrix}\longrightarrow CH\leqslant\begin{matrix}CH(OH)\cdot CO_2H\\ CH\cdot CO_2H\end{matrix}\longrightarrow$$

$$CH_2<\begin{matrix}\dot{C}(OH)\cdot CO_2H\\ \dot{C}H\cdot CO_2H\end{matrix}\longrightarrow CH\leqslant\begin{matrix}C(OH)\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}\longrightarrow CH_2<\begin{matrix}CO\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}$$

is proved by the fact that 1-bromo*cyclo*propane-1 : 2-dicarboxylic acid (IX), which, apparently, is the first product of ring-closure, when treated with a concentrated, methyl-alcoholic solution of potassium hydroxide, yields a mixture of the methoxy-acid (XII) and the ketonic acid (XIII) in about the same proportion as that obtained when ethyl dibromoglutarate is hydrolysed under comparable experimental conditions. The formation of these acids is therefore probably to be represented as follows:

$$CH_2<\begin{matrix}CHBr\cdot CO_2Et\\ CHBr\cdot CO_2Et\end{matrix}\longrightarrow CH_2<\begin{matrix}CBr\cdot CO_2H\\ CH\cdot CO_2H\end{matrix}\longrightarrow (XII.)$$

$$\swarrow$$

$$CH_2<\begin{matrix}C(OH)\cdot CO_2H\\ CH\cdot CO_2H\end{matrix}\longrightarrow CH_2<\begin{matrix}C(OH)_2\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}\longrightarrow (XIII.)$$

I wish to be allowed this opportunity of expressing my gratitude to Prof. J. F. Thorpe for his interest in these experiments and for the encouragement I have received from him.

Experimental.

(A) *Preparation of Glutaric Acid.*

An examination was made of the various methods hitherto proposed for preparing this substance. The oxidation of *cyclo*pentanone by nitric acid provides the quickest and cheapest method of obtaining the acid in quantity. From 1 kilogram of *cyclo*hexanol 300—350 grams of glutaric acid may be obtained after three operations, oxidation by nitric acid to adipic acid (*Bull. Soc. chim.*, 1908, **146**, 432), distillation of the latter with baryta (Friedländer, 1912—1914, 48, Fr. Pat. 33624), and oxidation of the distillate (*Annalen*, 1893, **275**, 320), all of which are easy to carry out with considerable amounts of material. The crude glutaric acid extracted from the oxidation product by means of benzene melted sharply at 95° after recrystallisation from chloroform.

(B) *Monobromination of Glutaric Acid.*

A mixture of glutaric acid (200 grams) and thionyl chloride (280 c.c.) was warmed until no more sulphur dioxide was generated. The product was heated at 60° before a naked arc light, while dry bromine (87 c.c.) was added in six equal portious at intervals timed to correspond with the rate of absorption.

Ethyl a-Bromoglutarate.

This ester was prepared by pouring the crude bromination product into ethyl alcohol, and was collected in ether after adding water. Traces of acidic products were removed by sodium carbonate, the extract was washed, dried, and the oil remaining after evaporation of the ether distilled several times, when the mono-bromo-ester, b. p. 142°/11 mm., was isolated, the yield being 50 per cent. of the theoretical (Found, Br = 29·9. $C_9H_{15}O_4Br$ requires Br = 30·0 per cent.).

(C) *Dibromination of Glutaric Acid.*

The dibromination was conducted exactly like the mono-bromination, except that 174 c.c. of bromine were used and the whole operation was conducted at 100°. The product was divided, part being poured into formic acid, and part into ethyl alcohol. In another experiment one portion was poured into methyl alcohol and another into *iso*propyl alcohol.

meso-*αα′-Dibromoglutaric Acid.*

The crystals which separated from the formic acid solution were collected and the mother liquors evaporated to dryness. The residual syrup on seeding with a crystal completely solidified. The crystalline material was washed with a small amount of a mixture of chloroform and light petroleum, and was then finely powdered, and extracted with boiling chloroform until the melting point of the undissolved portion was 165°. This, on recrystallising from a mixture of ether and chloroform, yielded *meso*dibromoglutaric acid. A further quantity was obtained by evaporating the chloroform extracts, treating the residue with the boiling solvent, and filtering the solution after cooling, when the *meso*-acid separated in dense, very hard prisms melting at 170° (Found, Br = 55·1. Calc., Br = 55·2 per cent.).

Racemic *αα′-Dibromoglutaric Acid.*

The residue obtained on evaporating the chloroform filtrate melted at 130—136°, and constituted about one-third of the original crystalline material. It was recrystallised alternately from chloroform and a mixture of acetone and benzene. Three crystallisations from each solvent yielded the *racemic* acid in a state of purity. The material isolated from the mother liquors, after re-extracting with boiling chloroform, was purified in the same way. The acid separated in heavy, oblique prisms presenting a curious, speckled appearance, owing to certain of the crystal facets transmitting practically the whole of the incident light. This property only became noticeable when the acid had been almost completely freed from the *meso*-isomeride, and may apparently be taken as a good indication of the purity of the specimen. The pure acid melted at 142° (Found: Br = 55·1. Calc.: Br = 55·2 per cent.).

Methyl αα′-Dibromoglutarate.

The preparation of this *ester* from the crude dibrominated product with the aid of methyl alcohol was similar to that of ethyl α-bromoglutarate. It boiled at 172°/32 mm., the yield being 85 per cent. of the theoretical (Found: Br = 50·1. $C_7H_{10}O_4Br_2$ requires Br = 50·3 per cent.). Only traces of acidic products were extracted by sodium carbonate.

Ethyl αα′-Dibromoglutarate.

The *ethyl* ester was obtained in equally satisfactory yield by pouring the dibromination product into ethyl alcohol. It was isolated like the methyl ester, and boiled at 174—175°/21 mm. (Found: Br = 46·3. $C_9H_{14}O_4Br_2$ requires Br = 46·2 per cent.).

iso*Propyl αα′-Dibromoglutarate.*

This *ester* was obtained in an analogous way, using *iso*propyl alcohol. It boiled at 195°/31 mm. (Found: Br = 42·8. $C_{11}H_{18}O_4Br_2$ requires Br = 42·8 per cent.).

(D) *Action of Dilute Alkalis on Ethyl α-Monobromoglutarate: Formation of α-Hydroxyglutaric Acid, its Lactonic Acid, and of* trans-cyclo*Propane*-1 : 2-*dicarboxylic Acid.*

Ten grams of ethyl α-bromoglutarate (section *B*) were boiled for twenty hours with 4·5 equivalents of a 2*N*-solution of sodium carbonate. The product was acidified, saturated with ammonium sulphate, and extracted with ether. The aqueous layer was evaporated to dryness, and the residue extracted with acetone.

α-Hydroxyglutaric Acid (I, p. 310).*

The residue from the acetone extract was mixed with some fresh acetone, when in the course of a few days crystals were deposited, further quantities being obtained by adding small amounts of benzene. The substance was recrystallised from moist ethyl acetate at the ordinary temperature, when it separated in large prisms, which melted with decomposition at 98—100°, and passed into the lactonic acid (Found: C = 40·4; H = 5·5. $C_5H_8O_5$ requires C = 40·5; H = 5·4 per cent.).

The acid does not appear to have been isolated previously in the pure condition, although several of its salts are known.

Lactonic Acid of α-Hydroxyglutaric Acid.

The acetone and benzene mother liquors from which α-hydroxyglutaric acid had separated were evaporated, and the residue left in an evacuated desiccator for three weeks. The cake of fine,

* Ethyl α-hydroxyglutarate has been prepared by directly esterifying the acid. It is a colourless, mobile liquid boiling at 143°/12 mm. (Found C = 52·8; H = 8·1. $C_9H_{16}O_5$ requires C = 52·9; H = 7·9 per cent.).

needle-shaped crystals into which it had changed was then recrystallised from a mixture of acetone and benzene at a low temperature. The pure substance melted at 50°, was very hygroscopic, and closely agreed in its properties with the acid described by Wolff (*Annalen*, 1890, **260**, 129) (Found: C=46·2; H=4·7. Calc.: C=46·1; H=4·6 per cent.).

trans-cyclo*Propane*-1 : 2-*dicarboxylic Acid* (III, p. 310).

The ethereal extract of the acidified product of hydrolysis was dried and evaporated, and the small residue treated with a drop of concentrated hydrochloric acid. The crystals which separated were drained, and, after recrystallisation from a few drops of water, identified with an authentic specimen of *trans-cyclo*propane-1 : 2-dicarboxylic acid by the method of mixed melting point (174°) (Found: C=45·7; H=4·8. Calc.: C=46·1; H=4·6 per cent.).

(E) *Action of Concentrated Alkalis on Ethyl α-Monobromoglutarate: Formation of α-Hydroxyglutaric Acid, its Lactonic Acid, Glutaconic Acid,* cis- *and* trans-cyclo-*Propanedicarboxylic Acids, and Paraconic Acid.*

Two hundred grams of ethyl α-bromoglutarate (section *B*) were heated to 100° and run in a thin stream into 1000 c.c. (2·7 × 3 equivalents) of a boiling 6*N*-methyl-alcoholic solution of potassium hydroxide. The mixture was boiled for thirty minutes, and then evaporated several times with water. The residue was dissolved in a slight excess of concentrated hydrochloric acid, and the organic acids extracted by means of ether and acetone. The product consisted of 70 grams of a syrup soluble in ether and 29 grams of a syrup sparingly soluble in ether, but readily so in acetone.

trans-cyclo*Propane*-1 : 2-*dicarboxylic Acid* (III, p. 310).

The syrup which was soluble in ether was allowed to crystallise as completely as possible, and the solid, consisting essentially of *trans-cyclo*propanedicarboxylic acid, drained on porous porcelain. The residual syrup was extracted by means of ether from the porous porcelain and digested with acetyl chloride for six hours. The excess of the reagent was evaporated, the residue dissolved in ether, and the solution extracted quickly with a dilute, aqueous solution of sodium hydroxide. The aqueous solution was acidified, concentrated, and extracted with ether. After removal of the

solvent, the residual syrup was esterified with ethyl alcohol and zinc chloride, the water formed in the reaction being carried away in a current of benzene vapour. After evaporating the excess of alcohol, the ester was repeatedly distilled (b. p. 230—240°), and was then hydrolysed by boiling with concentrated hydrochloric acid. The product, after most of the reagent had evaporated, was allowed to crystallise in an evacuated desiccator. The crystals, consisting of crude *trans-cyclo*propane-1 : 2-dicarboxylic acid, were freed from a small quantity of adhering syrup by draining on porous porcelain, and added to the first crop, the total weight of the crude, crystalline acid amounting to 34 grams. After recrystallisation from water, it melted at 175° (Found: C=46·1; H=4·7. Calc.: C=46·1; H=4·6 per cent. For the *silver* salt, found: Ag=62·6. Calc.: Ag=62·8 per cent.).

cis-cyclo*Propane*-1 : 2-*dicarboxylic Acid* (III, p. 310).

The ethereal solution of the anhydrides (p. 319) was dried and evaporated. The residue was boiled with water, and the clear solution evaporated in a vacuum over sulphuric acid. The stiff gum thus obtained (about 15 grams) exhibited no tendency to crystallise, and was therefore esterified with ethyl alcohol and zinc chloride in a current of benzene vapour. The ester was separated into two main fractions, the larger having b. p. 228—235°, and the smaller b. p. 242—247°, which were separately digested with an excess of a 3*N*-ethyl-alcoholic solution of potassium hydroxide. After evaporating the alcohol, an excess of hydrochloric acid was added, and the organic acids extracted with ether. The acid thus obtained from the fraction of lower b. p. solidified almost completely to a dense cake of crystals, which, on recrystallising from a mixture of acetone and benzene, melted at 139°. The acid was identified as *cis-cyclo*propane-1 : 2-dicarboxylic acid by analysis (Found: C=46·0; H=4·6. Calc.: C=46·1; H=4·6 per cent.), by the preparation of its anhydride (m. p. 76°), and by conversion into the *trans*-isomeride by heating with dilute sulphuric acid.

The acid obtained from the ester of higher b. p. gave, on analysis, figures agreeing closely with those required for *a-methoxyglutaric acid* (Found: C=44·4; H=6·2. $C_6H_{10}O_5$ requires C=44·4; H=6·2 per cent. For the *silver* salt, found: Ag=57·2. $C_6H_8O_5Ag_2$ requires Ag=57·4 per cent.). Unfortunately, the quantity was very small, and the acid could not be obtained in a crystalline form.

Glutaconic Acid (II, p. 310).

The presence of glutaconic acid in the ultimate residues obtained in the preparation of *trans-cyclo*propanedicarboxylic acid was demonstrated in the following way. The porous plates on which the second crop of *trans-cyclo*propanedicarboxylic acid had been drained were extracted with ether, and the residue from the ethereal extract digested for six hours with acetyl chloride containing phosphorus trichloride. After evaporating the excess of the reagent, the anhydrides were dissolved in benzene and treated with an excess of aniline. The crystalline product was washed with dilute hydrochloric acid, dissolved in a cold solution of sodium carbonate, and reprecipitated from the filtered solution by hydrochloric acid. Finally, it was recrystallised from a mixture of methyl alcohol and benzene. The pure substance melted at 134°, and was identified as the *cis*-semianilide of glutaconic acid by analysis (Found: C=64·6; H=5·5. Calc.: C=64·4; H=5·4 per cent.), by comparison with an authentic specimen, and by conversion by heating into the *trans*-isomeride (m. p. 167°), which was also identified by means of a genuine specimen (compare Bland and Thorpe, T., 1912, **101**, 857).

α-Hydroxyglutaric Acid and its Lactonic Acid.

The syrup insoluble in ether was first decolorised by digesting its solution in acetone with active charcoal. Preliminary experiments and analyses, particularly of the silver salts precipitated under varying conditions, having indicated, in addition to α-hydroxyglutaric acid and its lactonic acid, the presence of some other less easily hydrated lactonic acid, three-quarters of the total syrup was dissolved in moist ethyl acetate, warmed at 30°, and inoculated with a crystal of α-hydroxyglutaric acid. Crystallisation proceeded rapidly during the first day, and afterwards only slowly. The crystals were weighed from time to time, the solution being temporarily decanted for this purpose, and the calculated amount of water added after replacing the mother liquor. Finally, when crystallisation had ceased, the liquid was decanted, dried with anhydrous sodium sulphate, filtered, and replaced. The crystals, together with the dried mother liquor, were cooled in a freezing mixture for twelve hours, and then finally separated. The substance melted at 96—100° with decomposition, and consisted of almost pure α-hydroxyglutaric acid, evidently formed to a considerable extent by the gradual hydration of its lactonic acid. It was recrystallised for analysis from moist ethyl acetate (Found: C=40·35; H=5·55. Calc.: C=40·5; H=5·4 per cent.).

Paraconic Acid (IV, p. 311).

The solution in ethyl acetate was evaporated, and the residue triturated with a small quantity of chloroform. The crystals which separated were drained on porous porcelain and recrystallised from a mixture of chloroform and ether (Found: C=46·3; H=4·7. Calc.: C=46·1; H=4·6 per cent.). The acid melted at 57°, and its identity with paraconic acid was placed beyond doubt by converting it into citraconic anhydride by distillation, and identifying the citraconic acid derived from this product by direct comparison with a genuine specimen.

(F) *Action of Dilute Alkalis on the αα′-Dibromoglutaric Acids and their Esters: Formation of* meso- *and* racemic *αα′-Dihydroxyglutaric Acids, their Lactonic Acids, and* 1-*Bromo- and* 1-*Hydroxy*-cyclo*propane*-1:2-*dicarboxylic Acids.*

(a) *Hydrolysis of the* meso-*Dibromo-acid.*—Twenty-five grams of the *meso*-acid (section *C*) were boiled with 250 c.c. of a 2*N*-solution of sodium carbonate for 1·5 hours. As no material could be extracted by means of ether from the acidified solution, it was evaporated to dryness and the residue extracted with acetone. The syrup remaining after evaporating the acetone solidified completely after a few days.

meso-*αα′-Dihydroxyglutaric Acid* (V, p. 314).

The preceding solid was dissolved in boiling acetone, and the *meso*-dihydroxy-acid, which was only sparingly soluble in the cold solvent, was deposited on cooling in thick, prismatic crystals which adhered tenaciously to the walls of the tube. The substance melts at 162° and immediately evolves water-vapour. It is very soluble in water and in methyl and ethyl alcohols, moderately soluble in boiling acetone, sparingly so in ethyl acetate, and practically insoluble in chloroform, ether, and benzene (Found, C=36·7; H=5·2. $C_5H_8O_6$ requires C=36·6; H=4·9 per cent.).

trans-*Lactonic Acid of αα′-Dihydroxyglutaric Acid* (VI, p. 314).

(i) The acetone solution from which the dihydroxy-acid had crystallised deposited, after the addition of successive small portions of benzene, a small quantity of the same dihydroxy-acid and also a considerable amount of a lactonic acid melting at 150°.

(ii) On heating the *meso*-dihydroxy-acid at 165° for a few

minutes a colourless, very viscous gum was formed. After some time this completely solidified to a crystalline substance, m. p. 148·5—150°, which was immediately soluble in a cold solution of sodium carbonate and so could not have contained any anhydride or dilactone. It was crystallised for analysis from ethyl acetate (Found, C=41·2; H=4·25. $C_5H_6O_5$ requires C=41·1; H=4·1 per cent. For the *silver* salt: Found, Ag=42·6. $C_5H_5O_5Ag$ requires Ag=42·7 per cent.).

The lactonic acid prepared by either of these methods yielded the *meso*-dihydroxy-acid on hydration with boiling water, and the dianilide and di-*p*-toluidide of this acid on heating with aniline and *p*-toluidine respectively.

meso-*Dianilide*, $CH_2[CH(OH)\cdot CO\cdot NHPh]_2$.—This derivative was prepared by boiling either the *meso*-acid or the *trans*-lactonic acid with excess of aniline for a few seconds. The anilide crystallised on cooling, and was purified by triturating with dilute hydrochloric acid and recrystallising from ethyl alcohol. It separated in very thin, glistening plates which melted without decomposition at 223°, and were soluble only in a large volume of hot alcohol (compare the *racemic* anilide) (Found, C=64·75; H=5·7. $C_{17}H_{18}O_4N$ requires C=65·0; H=5·7 per cent.).

meso-*Di*-p-*toluidide*, $CH_2[CH(OH)\cdot CO\cdot NH\cdot C_7H_7]_2$.—The toluidide was prepared in an analogous way, and, like the anilide, crystallised from the fused *p*-toluidine on cooling. After recrystallisation from a large amount of ethyl alcohol it melted at 232° without decomposition, and was similar in appearance and solubility to the anilide (Found, C=66·5; H=6·5. $C_{19}H_{22}O_4N_2$ requires C=66·7; H=6·4 per cent.).

(b) *Hydrolysis of the* Racemic *Dibromo-acid*.—Ten grams of the *racemic* acid (section *C*) were boiled with 100 c.c. of a 2*N*-solution of sodium carbonate for one and a-half hours. Extraction with ether did not remove any material from the acidified solution, which was therefore evaporated to dryness and the residue extracted with acetone. In the course of a few days the syrup which remained when the acetone had evaporated solidified almost completely.

Racemic *αα′-Dihydroxyglutaric Acid* (VII, p. 314).

A portion of this material was boiled with water in the presence of a little charcoal, and the filtered solution allowed to crystallise at the ordinary temperature. The dihydroxy-acid which separated changed into the *cis*-lactonic acid when left in the steam-oven. On heating in a tube it melted at about 125° (the exact temperature

depending on the rate of heating), eliminating water, and yielding the same lactonic acid (Found, C = 36·4; H = 5·1. $C_6H_8O_6$ requires C = 36·6; H = 4·9 per cent.).

cis-*Lactonic Acid of αα'-Dihydroxyglutaric Acid* (VIII, p. 314).

(i) The solid residue from the acetone extract appeared to consist mainly of this lactonic acid, and yielded it in the pure condition when recrystallised from a mixture of acetone and benene. It then melted at 168°.

(ii) The *racemic* dihydroxy-acid on heating at 135° for a few minutes gave a quantitative yield of the pure lactonic acid. The product was immediately soluble in a cold solution of sodium hydrogen carbonate, and therefore contained no anhydride or dilactone. It melted at 166—168°, and after crystallisation from a mixture of acetone and benzene at 168° (Found, C = 41·0; H = 4·1. $C_5H_6O_5$ requires C = 41·1; H = 4·1 per cent. For the *silver* salt: Found, Ag = 42·55; $C_5H_5O_5Ag$ requires Ag = 42·7 per cent.).

The lactonic acid obtained by both these methods yielded the same *racemic* dihydroxy-acid on hydration with boiling water, and the dianilide and di-*p*-toluidide of this acid when heated with the appropriate base.

Racemic *Dianilide*, $CH_2[CH(OH)\cdot CO\cdot NHPh]_2$.—This substance was prepared by boiling either the *racemic* dihydroxy-acid or the *cis*-lactonic acid for a few seconds with an excess of aniline. The anilide did not crystallise on cooling (compare the *meso*-anilide), but was precipitated by adding dilute hydrochloric acid. It was recrystallised from a small amount of ethyl alcohol and obtained in stout, oblique prisms melting at 156° without decomposition. Unlike the *meso*-isomeride, it is very soluble in hot alcohol (Found, C = 65·3; H = 5·8. $C_{17}H_{18}O_4N_2$ requires C = 65·0; H = 5·7 per cent.).

Racemic *Di*-p-*toluidide*, $CH_2[CH(OH)\cdot CO\cdot NH\cdot C_7H_7]_2$. — The toluidide was obtained in a similar way, using *p*-toluidine in place of aniline. It separated from alcohol in rather slender needles melting without decomposition at 179°. Like the anilide, it is very soluble in boiling alcohol (compare the *meso*-toluidide) (Found, C = 66·6; H = 6·4. $C_{19}H_{22}O_4N_2$ requires C = 66·7; H = 6·4 per cent.).

(c) *Hydrolysis of the Methyl and Ethyl Dibromo-esters.*—One decigram-molecule of methyl or ethyl dibromoglutarate was boiled with 250 c.c. of a 2*N*-solution of sodium carbonate for twenty hours. The clear solution was acidified with 50 c.c. of concentrated hydrochloric acid, saturated with ammonium sulphate, and extracted

twenty times with an equal volume of ether. The aqueous residue was then evaporated to dryness and extracted with acetone.

The *hydroxylation products* extracted with acetone evidently consisted almost entirely of a mixture of *meso-* and *racemic* dihydroxyglutaric acids and their respective lactonic acids, as on boiling with an excess of aniline it yielded twice its weight of a mixture of two anilides, which were readily separated by crystallisation from alcohol and identified with the *meso-* and *racemic* anilides mentioned above.

1-*Bromo*cyclo*propane*-1:2-*dicarboxylic Acid* (IX, p. 314).

The ethereal extract on evaporation yielded a crystalline residue which melted at 165—170°, and after two crystallisations from a mixture of ether and chloroform at 172°. The acid separated in dense, thick prisms. The presence of the halogen could not be detected by boiling in an open tube with nitric acid and silver nitrate, and in a sealed tube the decomposition had to be carried out at an unusually high temperature in order to obtain the correct amount of silver bromide. The silver salt of the acid also exhibited extraordinary stability. When boiled with water in direct sunlight it remained quite white, and in solution in dilute nitric acid it could be boiled without any separation of silver bromide taking place. Taking advantage of this fact, the silver was estimated by direct precipitation with hydrochloric acid. The bromo-acid also appeared to be very stable towards concentrated hydrochloric acid and an alkaline solution of permanganate, which it decolorised only slowly even on boiling (Found, C=28·9; H=2·5; Br=37·8. $C_5H_5O_4Br$ requires C=28·7; H=2·4; Br=38·2 per cent. For the *silver* salt: Found, Ag=51·3. $C_5H_3O_4BrAg$ requires Ag=51·1 per cent.). The action of concentrated and dilute alkalis is described below.

Boiling with aniline appeared to bring about some deep-seated decomposition, and a dianilide was not obtained. A characteristic *aniline* salt was, however, prepared by mixing ethereal solutions of the acid and the base. It separated in rosettes of needles which melted at 130° (Found, C=51·4; H=4·85. $C_{17}H_{19}O_4N_2Br$ requires C=51·6; H=4·8 per cent.).

(d) *Hydrolysis of the* iso*Propyl Dibromo-ester.*—This ester was not acted upon by 2*N*-sodium carbonate very quickly. A decigram-molecule of the ester was boiled with 250 c.c. of this reagent for two hundred hours, and the small quantity of oil which still remained was extracted with ether. The aqueous layer was acidified with 50 c.c. of concentrated hydrochloric acid, saturated with

ammonium sulphate, and extracted thirty times with an equal volume of ether. The aqueous solution was then evaporated to dryness and the residue extracted with acetone.

The *hydroxylation products* extracted by acetone were dealt with as described in sub-section (*c*) and yielded similar results.

The *cyclic products* extracted with ether crystallised rapidly on evaporating the solvent, and were freed from gummy impurities by draining on porcelain and washing with cold chloroform. The residue consisted essentially of a mixture of two acids, one of which was easily soluble, and one almost insoluble, in dry ether. The former on purification melted at 172°, contained bromine, and was easily identified with the above-mentioned bromo*cyclo*propanedicarboxylic acid. The latter proved to be *cyclo*propanol-1 : 2-dicarboxylic acid.

cyclo*Propanol*-1 : 2-*dicarboxylic Acid* (X, p. 314).

(i) This acid was obtained by recrystallising the portion of the ether extract insoluble in dry ether from a mixture of acetone and benzene.

(ii) It was also prepared by boiling the bromo*cyclo*propanedicarboxylic acid with excess of 2*N*-sodium carbonate for five hundred hours. On acidifying, concentrating, and extracting thoroughly with ether, the acid was obtained together with a small quantity of the undecomposed bromo-acid, which was easily removed with dry ether. The residue was recrystallised from a mixture of acetone and benzene, and a 50 per cent. yield of the pure hydroxy-acid obtained (Found, C = 41·2; H = 4·2. $C_5H_6O_5$ requires C = 41·1; H = 4·1 per cent. For the *silver* salt: Found, Ag = 59·9. $C_5H_4O_5Ag_2$ requires Ag = 60·0 per cent.).

The hydroxy-acid crystallised in short needles melting at 206—210°. It appeared fairly stable to boiling 20 per cent. hydrochloric acid, an alkaline solution of permanganate, and a dilute aqueous solution of sodium hydroxide. The action of concentrated sulphuric acid is described in section *H*, and that of a concentrated, methyl-alcoholic solution of potassium hydroxide in section *G*.

(G) *Action of Concentrated Alkali on Ethyl αα′-Dibromoglutarate. Formation of* meso- *and* racemic *αα′-Dihydroxyglutaric Acids, their Lactonic Acids, Methoxy*cyclo*propane*-1 : 2-*dicarboxylic Acid, and α-Ketoglutaric Acid.*

Two hundred grams of ethyl dibromoglutarate were heated to 100° and poured in a thin stream into 1040 c.c. (2·7 × 4 molecules)

of a boiling, 6N-methyl-alcoholic solution of potassium hydroxide. When the violence of the reaction had subsided the product was heated for thirty minutes, evaporated twice with water, and the residue acidified with concentrated hydrochloric acid. On extracting the acid products, 77 grams of a syrup completely soluble in ether were obtained, whilst the material on the filters, when collected in acetone, yielded 8 grams of a syrup insoluble in ether.

The syrup soluble in ether consisted of a mixture of methoxy*cyclo*propane-1 : 2-dicarboxylic acid and α-ketoglutaric acid, and the insoluble syrup of hydroxylation products. When either the bromo- or hydroxy-*cyclo*propanedicarboxylic acid (section F) was used in place of the dibromo-ester only a soluble syrup was obtained consisting of the same two acids in about the same proportions.

The *hydroxylation products* were treated as described in section F (p. 324) with similar results.

*Methoxy*cyclo*propane*-1 : 2-*dicarboxylic Acid* (XII, p. 315).

The soluble syrup soon began to crystallise, and after two weeks a thick crust of dense, prismatic crystals had separated on the walls of the dish, which was inverted for several days to drain off the residual gum. The crystals then melted at 119—120°, and, after recrystallisation from a mixture of benzene and acetone, sharply at 121° (Found, C=44·95; H=5·0. $C_6H_8O_5$ requires C=45·0; H=5·0 per cent. For the *silver* salt: Found, Ag=57·6. $C_6H_6O_5Ag_2$ requires Ag=57·7 per cent.). When the methoxy-acid was warmed with concentrated sulphuric acid, oxidation occurred, and succinic acid was isolated from the product. Towards an alkaline solution of permanganate the acid exhibited the extraordinary stability characteristic of many acids of the *cyclo*propane series.

Ethyl α-Ketoglutarate.

The gum drained from the methoxy-acid was esterified with ethyl alcohol and sulphuric acid, and the acid esters were separated in the usual manner and re-esterified. On distillation, apart from a small fraction of low b. p., from which a further quantity of the preceding methoxy-acid was obtained on hydrolysis, by far the greater portion of the neutral ester was isolated as ethyl α-ketoglutarate, b. p. 152—155°/27 mm. (Found, C=53·3; H=7·1. Calc., C=53·5; H=6·9 per cent.), since on hydrolysis with hydrochloric acid it gave a quantitative yield of α-ketoglutaric acid, and on shaking with an aqueous solution of semicarbazide acetate a crystalline, semicarbazone melting at 114° was obtained. (The b. p. of the ester

is given as 160°/23 mm. by Wislicenus and Waldmüller, *loc. cit.*, and as 114°/13 mm. by Blaise and Gault, *loc. cit.*; the latter also record 114° as the m. p. of its semicarbazone. A similar difficulty encountered in identifying the ketonic acid is mentioned below.)

a-*Ketoglutaric Acid* (XIII, p. 315).

The ketonic ester was readily soluble in cold, concentrated hydrochloric acid. The solution was boiled for two minutes and then evaporated. The colourless, syrupy residue, on touching with a rod, immediately set to a cake of crystals, which, without purification, melted at 111—113°. After two recrystallisations from a mixture of acetone and benzene, the acid melted at 113·5°. It was identified as a-ketoglutaric acid by analysis (Found: C=40·9; H=4·2. Calc.: C=41·1; H=4·1 per cent.) and by the preparation of its oxime, which melted at 140° and, on boiling first with water and then with a solution of potassium hydroxide, gave succinic acid, with the elimination of carbon dioxide and ammonia. The semicarbazone and phenylhydrazone were also prepared. The former separated from warm water in colourless needles melting with decomposition at 220°, and the latter from alcohol as pale buff-coloured plates, which melted and decomposed at 152°. The ketonic acid developed a dull crimson colour with a solution of ferric chloride in dilute alcohol (Wislicenus and Waldmüller, *loc. cit.*, quote 115—116° as the melting point of the ketonic acid and 152—153° as that of its phenylhydrazone. Blaise and Gault, *loc. cit.*, give 113° as the melting point of the ketonic acid, 140° as that of the oxime, 220° as that of the semicarbazone, and 260° as that of the phenylhydrazone. The same authors describe the colour given with ferric chloride as yellowish-green). In spite of these differences, there would seem to be no douht as to the identity of the acid and of its ester.

(H) *Action of Concentrated Sulphuric Acid on* cyclo*Propanol-1 : 2-dicarboxylic Acid: Formation of* cyclo*Propanone together with Propionic and Succinic Acids.*

A solution of the *cyclo*propanoldicarboxylic acid in about five times its weight of concentrated sulphuric acid was warmed under reflux, whereby carbon monoxide, and subsequently carbon dioxide and sulphur dioxide, were rapidly evolved. The solution was poured into six times its volume of water and distilled in a current of steam.

cyclo*Propanone* (XI, p. 314).

The earlier fractions of the distillate had a faint ketonic odour, and contained almost the whole of the ketone. They were shaken with calcium carbonate to neutralise a trace of volatile acid, and then redistilled. Again the ketone was concentrated into the first fraction, but it was too soluble in water, and the quantity present too small, for a complete separation by fractional distillation to be possible. It was therefore isolated in the form of its *semicarbazone*, which separated from ethyl alcohol in short, colourless needles melting and decomposing at 230—232°. The yield, calculated on the *cyclo*propanoldicarboxylic acid, was 8 per cent. of the theoretical (Found: C=42·4; H=6·3; N=37·5. $C_4H_7ON_3$ requires C=42·5; H=6·2; N=37·2 per cent.).

The *fission products*, propionic acid and succinic acid, were readily isolated by continuing the distillation in steam. The distillate was neutralised and evaporated. The organic acids regenerated from the residue were converted into their anilides, which were crystallised from dilute alcohol. Propionanilide, which formed the main constituent, separated in prisms melting at 104°, and was identified by comparison with an authentic specimen and by analysis (Found: *C*=72·25; *H*=7·6. Calc.: *C*=72·5; *H*=7·4 per cent.). Succinic acid was isolated from the liquid in the distilling flask by extraction with ether. It was identified by direct comparison with a genuine specimen and by analysis (Found: C=41·0; H=5·1. Calc.: C=40·7; H=5·1 per cent.).

A considerable proportion of the expense of this research has been met by a grant from the Chemical Society, to whom my thanks are due.

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SOUTH KENSINGTON. [*Received, December 28th*, 1920.]

XLI.—*The Mechanism Underlying the Reaction between Ethyl Cyanoacetate and Tautomeric Substances of the Keto-enol Type.*

By CHRISTOPHER KELK INGOLD.

THE condensation of ethyl cyanoacetate with ketones has been the subject of numerous investigations. Usually, the first product which can be isolated is an unsaturated cyano-ester, in which the

double bond may be situated in either the $\alpha\beta$- or the $\beta\gamma$-position with respect to the carboxyl group. Acetone, for example, yields an *$\alpha\beta$-unsaturated condensation* product, whilst *cyclo*hexanone gives mainly a cyano-ester, in which the double bond occupies the $\beta\gamma$-position (Komppa, *Ber.*, 1900, **33**, 3530; Harding, Haworth, and Perkin, T., 1908, **93**, 1944).

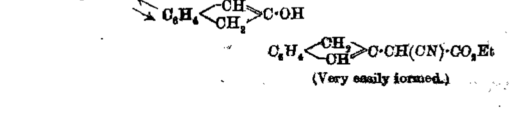
$$Me_2CO + CH_2(CN)\cdot CO_2Et \longrightarrow Me_2C{:}C(CN)\cdot CO_2Et$$

$$CH_2{<}{}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}CO + CH_2(CN)\cdot CO_2Et \longrightarrow CH_2{<}{}^{CH_2\cdot CH_2}_{CH_2-CH}{>}C\cdot CH(CN)\cdot CO_2Et.$$

The latter type of reaction appears to be that most frequently met with, and it is possible to ascribe the production of α-cyano-β-methylcrotonic ester from acetone to the instability of the $\beta\gamma$-unsaturated isomeride that is intermediately formed (compare, however, p. 335). In such cases, a second molecule of ethyl cyanoacetate may enter into reaction, the product being a derivative of glutaric acid (*loc. cit.*):

$$Me_2C{:}C(CN)\cdot CO_2Et + CH_2(CN)\cdot CO_2Et \longrightarrow Me_2C{<}{}^{CH(CN)\cdot CO_2Et}_{CH(CN)\cdot CO_2Et}.$$

With regard to the primary condensation, there can be no doubt but that it is the enolic modification of the ketone which actually enters into the reaction, because ketones, such as benzophenone, of which no enolic modification can exist, fail to react (Haworth, T., 1909, **95**, 480), whilst others condense with a readiness apparently proportionate to their capacity for tautomeric change; thus, α-hydrindone condenses moderately well, and β-hydrindone, in which the tautomeric system is duplicated in such a way as to prolong the enolic phase, enters into condensation with great rapidity, even under much milder conditions (Ingold and Thorpe, T., 1919, **115**, 145):



Again, tautomeric ketonic esters, provided they are not sufficiently acidic to cause the dissociation of the sodium compound of ethyl cyanoacetate, readily yield condensation products with this substance; but once the tautomeric character of the ketonic ester has been destroyed, for example, by alkylation, then condensation can no longer be effected. Thus, ethyl acetoacetate yields ethyl α-cyano-β-methylglutaconate,

$$CO_2Et\cdot CH{:}CMe\cdot OH + CHNa(CN)\cdot CO_2Et \longrightarrow CO_2Et\cdot CH{:}CMe\cdot CNa(CN)\cdot CO_2Et + H_2O,$$

whilst ethyl dimethylacetoacetate, $CH_3\cdot CO\cdot CMe_2\cdot CO_2Et$, shows no tendency to condense (Rogerson and Thorpe, T., 1905, **87**, 1685). There are many similar examples on record.

Although, however, it is almost certain that ketones only condense with cyanoacetic ester by virtue of their capacity to pass into their enolic modifications, the reason why this should be the case is still obscure, and no evidence appears to have been offered hitherto on the interesting, if intricate, question thus raised.

The problem is to discover wherein lies the cause of the reactivity of the enolic forms. Broadly speaking, there are two possibilities. The equation just given for the example afforded by ethyl acetoacetate suggests that the prime reaction consists in the elimination of water through the union of the hydroxyl group of the enolised substance with the reactive hydrogen atom of the cyano-ester. This view appears to be the one which, in default of direct evidence either for or against it, has gained acceptance (*loc. cit.*). It is possible, however, that the reactive feature of the enolic substance is not the hydroxyl group, but the double bond. The direct addition of ethyl sodiocyanoacetate would then be the initial reaction, the elimination of water being a subsequent occurrence. Illustrating by the same example, ethyl acetoacetate would first be converted into a hydroxy-cyano-ester, which would then eliminate water:

$$CO_2Et\cdot CH{:}CMe\cdot OH + CHNa(CN)\cdot CO_2Et \longrightarrow CO_2Et\cdot CH_2\cdot CMe(OH)\cdot CNa(CN)\cdot CO_2Et \longrightarrow CO_2Et\cdot CH{:}CMe\cdot CNa(CN)\cdot CO_2Et + H_2O.$$

To obtain a correct understanding of such an important type of reaction is obviously most desirable, and it seemed that a decision might best be reached by eliminating alternately the two possibilities. Thus, one might first try to condense esters in which there is a double bond, but no hydroxyl group; in this case, a reaction of the first type is impossible. Secondly, one might employ esters containing a hydroxyl group, but no double bond;

in this case the possibility of the occurrence of a reaction of the second type would be eliminated.

It is well known that unsaturated esters (not containing a hydroxyl group in a position adjacent to the double bond) react with ethyl cyanoacetate to form additive products. The corresponding investigation of esters of hydroxy-acids (not containing a double bond) has not previously been undertaken, and has, therefore, in view of its theoretical interest, now been commenced by a careful examination of a number of typical cases.

It may be stated at once that the evidence which has been obtained is strongly in favour of the second suggestion, namely, in all these cases the unsaturated linking is responsible for the initial condensation, and the elimination of water is a subsequent effect. Although the number of hydroxy-esters investigated is only nine, the results obtained point consistently to the same conclusion.

The formulæ of the hydroxy-esters which have been examined are given in the following tables.

TABLE I.

Monocarboxylic Esters.

	α-Hydroxy-esters.	β-Hydroxy-esters.
Primary	$CH_2(OH)\cdot CO_2Et$	$CH_2(OH)\cdot CH_2\cdot CO_2Et$
Secondary ...	$CHMe(OH)\cdot CO_2Et$	$CHMe(OH)\cdot CH_2\cdot CO_2Et$
Tertiary	$CMe_2(OH)\cdot CO_2Et$	—

TABLE II.

Dicarboxylic Esters.

	α-Hydroxy-esters.	β-Hydroxy-esters.	α- and β- (mixed type) Hydroxy-esters.
Secondary	$CH(OH)\cdot CO_2Et$ $CH_2\cdot CH_2\cdot CO_2Et$	$CH_2\cdot CO_2Et$ $CH(OH)\cdot CH_2\cdot CO_2Et$	$CH(OH)\cdot CO_2Et$ $CH_2\cdot CO_2Et$
Tertiary	—	—	$CH_2\cdot CO_2Et$ $C(OH)\cdot CO_2Et$ $CH_2\cdot CO_2Et$

Glycollic ester, the simplest of all these hydroxy-esters, was the only one which yielded no trace of condensation product with ethyl sodiocyanoacetate under conditions which gave positive results with all the other esters investigated. The reason for this is readily perceived if the tables of formulæ are examined; glycollic ester is the only ester which cannot pass by loss of water into an unsaturated compound.

The other three α-hydroxy-esters all gave abnormal condensation products, such as could only have been derived by the direct addition of ethyl sodiocyanoacetate to the corresponding unsaturated compound; for example, lactic ester gave ethyl α-cyanoglutarate, from which glutaric acid was obtained by hydrolysis. The process must therefore be formulated thus:

$$CH_3\cdot CH(OH)\cdot CO_2Et \longrightarrow CH_2{:}CH\cdot CO_2Et \longrightarrow \begin{matrix} CH_2\cdot CH_2\cdot CO_2Et \\ | \\ CH(CN)\cdot CO_2Et \end{matrix} \longrightarrow \begin{matrix} CH_2\cdot CH_2\cdot CO_2H \\ | \\ CH_2\cdot CO_2H \end{matrix}$$

The product, if formed from the lactic and sodiocyanoacetic esters by the direct elimination of water, should give, on hydrolysis, methylsuccinic acid, no trace of which, however, was obtained. Similarly, α-hydroxy*iso*butyric ester, when treated in the same way, gave α-methylglutaric acid; if the hydroxy-ester had condensed by the direct elimination of water through the union of its hydroxyl group with the reactive hydrogen atom of ethyl sodiocyanoacetate, the final product should have been *as*-dimethylsuccinic acid. No trace of this substance could be detected, and the reaction must therefore be regarded as dependent on the production of an unsaturated ester, as in the case of ethyl lactate illustrated above. In the same way, ethyl α-hydroxyglutarate gave finally methanetriacetic acid, whilst no trace of the isomeric *n*-butane-αβδ-tricarboxylic acid could be isolated.

It is well known that esters of β-hydroxy-acids are converted by loss of water into unsaturated compounds much more readily than esters of α-hydroxy-acids. In agreement with the contention made in this paper, therefore, is the fact that the yields obtained in the condensations with the α-hydroxy-esters were, on the whole, much smaller than those with the β-hydroxy-esters. In the former cases, a large quantity of the unchanged hydroxy-ester was usually recovered, whilst with the β-hydroxy-esters the recovered material never exceeded 10 per cent. of that used. Further confirmation of the matter is obtained by comparing the α-hydroxy-esters amongst themselves. Whilst glycollic ester gave no yield, lactic and α-hydroxyglutaric esters gave only very poor yields. α-Hydroxy*iso*butyric ester, on the other hand, gave a moderately good yield. These results are clearly in harmony with the general thesis, inasmuch as glycollic ester is incapable of yielding an unsaturated ester, lactic and α-hydroxyglutaric esters have never been observed to do so, whilst, on the other hand, α-hydroxy*iso*butyric ester, as Frankland and Duppa have shown (*Annalen*, 1865, **32**, 12), somewhat readily eliminates water and yields an unsaturated derivative.

Next, turning to the β-hydroxy-esters, of which, if the esters of mixed type are included, five examples have been examined, the sole product in three cases is an ester in which the cyanoacetic residue directly replaces the hydroxyl group. This at first sight appears remarkable. The esters which behave thus are ethyl hydracrylate, β-hydroxybutyrate, and malate. However, an inspection of their formulæ and of those of the products obtained from them shows that the latter are actually the substances the formation of which should be expected by the addition of ethyl cyanoacetate to the appropriate, unsaturated derivative. The occurrence of these apparently exceptional cases is, therefore, in reality a strong argument in favour of the general scheme by which all the reactions are explained. Hydracrylic ester, consequently, gives, after condensation and hydrolysis, glutaric acid; β-hydroxybutyric ester gives β-methylglutaric acid, and malic ester tricarballylic acid, the reactions, for example, in the first-mentioned case, being formulated thus:

$$CH_2(OH){\cdot}CH_2{\cdot}CO_2Et \longrightarrow CH_2{:}CH{\cdot}CO_2Et \longrightarrow$$

$$\begin{matrix} CH_2{\cdot}CH_2{\cdot}CO_2Et \\ | \\ CH(CN){\cdot}CO_2Et \end{matrix} \longrightarrow \begin{matrix} CH_2{\cdot}CH_2{\cdot}CO_2H \\ | \\ CH_2{\cdot}CO_2H \end{matrix}$$

The condensation of β-hydroxyglutaric ester supplied very direct evidence of the intermediate formation of unsaturated compounds in these reactions. This experiment was performed in connexion with an entirely different investigation, and the details need not be entered into now, but from the viewpoint of the present discussion the item of interest is that it is possible to isolate from the product of the reaction a small amount of the intermediate, unsaturated substance, the formation of which is demanded by the hypothesis here offered.

Finally, there is the case of ethyl citrate. This condensation also was tried in connexion with another research, and the results, therefore, need not be described in detail. It suffices to point out that if citric ester condenses by the direct elimination of its hydroxyl group with a hydrogen atom of cyanoacetic ester, the product on hydrolysis should yield methanetetra-acetic acid. Now in the corresponding condensation with the unsaturated ester, no trace of an ester yielding this acid is produced, a mixture of two entirely different acids being obtained. It is impossible, therefore, to overlook the significance of the fact that the condensation with citric ester yields a mixture of the same two acids in similar proportions.

The necessity for the intermediate production of an unsaturated substance is not confined to condensations of ethyl cyanoacetate

with ketones and hydroxy-compounds. Even certain halogen derivatives, for example, ethyl β-chlorotricarballylate, appear to react by a similar mechanism, though such cases are very much rarer than those involving condensations with ethyl malonate. This is probably due to the fact that a small amount of alkali is necessary to eliminate the halogen (the reactions proceeding in a cycle), and, whilst a solution of ethyl sodiomalonate in 99·8 per cent. alcohol is faintly alkaline, an alcoholic solution of ethyl sodiocyanoacetate remains neutral, even on dilution with water (Thorpe, T., 1900, **77**, 923). It remains true, however, that by far the greater number of condensations of halogenated esters with ethyl sodiocyanoacetate pursue a course similar to the ordinary process of alkylation.

It seems curious that halogen compounds should thus be ranged into two classes (albeit of such unequal membership), and that these should react so differently with ethyl cyanoacetate. There can be no doubt, however, as to the fact, and it is possible that the difference is in certain respects similar to that which appears to exist between the condensations of aldehydes and of ketones. That the condensation of aldehydes with ethyl sodiocyanoacetate and similar substances depends on a different mechanism from that of ketones is shown by many reactions, amongst which may be mentioned the formation of saturated condensation products, of two substances, one of which has become oxidised at the expense of the other, and of stable alcohols, into the production of which several molecules of the aldehyde may enter; also, the extraordinary reactivity of aromatic aldehydes (which cannot form an unsaturated derivative), not only towards substances of a reactive nature like ethyl cyanoacetate, but also towards simple esters such as ethyl acetate, and towards aromatic compounds which may be neither esters nor nitriles, and may even be basic in character (Haworth, T., 1909, **95**, 480; Guareschi, *Atti R. Accad. Sci. Torino*, 1896—1897, **32**, 415; 1898—1899, **34**, 565; Henry, *Compt. rend.*, 1895, **120**, 1265; *Rec. trav. chim.*, 1897, **17**, 189; Piloty, *Ber.*, 1897, **30**, 3161; Boehm, *Ber.*, 1904, **37**, 4461; Simon, *Annalen*, 1903, **329**, 19; Day and Thorpe, T., 1920, **117**, 1465). Explanations for many of these peculiarities may easily be devised on the assumption that aldehydes react in an unstable form containing bivalent carbon, R·C(OH):, to which, it is necessary to observe, no analogy is possible with ketones.

Finally, with regard to the conditions determining the position of the double bond in the condensation products, it is of interest to notice that, in the condensation with *cyclo*hexanone mentioned on p. 330, there is formed, together with 93 per cent. of the

$\beta\gamma$-unsaturated cyano-ester, 7 per cent. of the $\alpha\beta$-unsaturated isomeride. This is evidently a result of the dual mode of dehydration of the hydroxy-ester, which is assumed to be formed initially by the direct addition of ethyl cyanoacetate to the enolic modification of the ketone. The closely analogous hydroxy-ester, prepared by treating *cyclo*hexanone by Reformatsky's method witb ethyl bromoacetate and zinc, has been found by Wallach (*Annalen*, 1907, **353**, 292) to yield on dehydration a very similar mixture of unsaturated esters containing 95 per cent. of the intra-cyclic and 5 per cent. of the semi-cyclic derivative, a fact in excellent accord with the mechanism suggested.

EXPERIMENTAL.

Condensation of Esters of Hydroxy-acids with Ethyl Sodio-cyanoacetate.

General Method.—To a solution of sodium ethoxide, obtained by dissolving 11·5 grams of sodium in 150 grams of ethyl alcohol, 56·5 grams of ethyl cyanoacetate were added. A solution of the hydroxy-ester (0·5 gram-mol. in 50 grams of alcohol) was then mixed with the suspension of the sodio-compound, and the whole heated on a steam-bath for thirty-six hours. The product was poured into water, and, after the addition of excess of hydrochloric acid, extracted with ether. The extract was washed with a solution of sodium carbonate and with water, and was then dried and distilled, finally under diminished pressure. By this means, the unchanged hydroxy-ester was easily separated from the neutral condensation product.

The sodium carbonate extract was acidified with hydrochloric acid, and the acidic product extracted with ether.

The neutral condensation product, after being distilled, was hydrolysed by the following method. It was first mixed with an equal volume of concentrated sulphuric acid, the temperature being kept below 30° during the process. After remaining overnight, the viscous liquid was treated with just sufficient water to cause a slight precipitation of oil, and tbe turbid solution was heated until carbon dioxide ceased to be evolved and no oil separated when a specimen was cooled. The whole solution was then cooled, diluted with an equal volume of water, and boiled for five hours to expel ethyl alcohol. After cooling, the solution was saturated with ammonium sulphate and exhaustively extracted with ether free from alcohol. From the extract, the appropriate polybasic acid was obtained in an almost pure state.

The acidic condensation product was usually divided into two

portions, one of which, in quantities of about 4 grams at a time, was distilled under diminished pressure, the distillation being completed as rapidly as possible after most of the carbon dioxide had been evolved. The distillate usually contained acidic products, principally the hydroxy-acid corresponding with the original ester or the unsaturated acid derived therefrom by dehydration, and was therefore dissolved in ether and washed with a solution of sodium carbonate. The ethereal solution was dried and evaporated, and the residual oil distilled under diminished pressure. This distillation always proceeded quietly and without any appreciable decomposition. The cyano-ester so obtained was hydrolysed by tbe same method as has been described for the hydrolysis of the neutral condensation product.

The second portion of the acidic condensation product was completely hydrolysed. It was mixed with an equal volume of cold, concentrated sulphuric acid, and the mixture allowed to remain at the ordinary temperature for two hours while carbon dioxide was (usually) evolved. The product was diluted with an equal volume of water, and, after the evolution of gas caused by this operation had abated, boiled for two hours or until it showed signs of darkening. After cooling, the solution was diluted to twice its volume with water, and boiled for five hours. The mixture of acids extracted from this solution with ether was, while still in the syrupy state, re-esterified by heating for three hours with ethyl alcohol (3 parts) and concentrated sulphuric acid (2 parts), and the esters isolated by diluting with water and extracting with ether. The acid esters, removed by washing the extract with a solution of sodium carbonate, were re-extracted after acidification of the washings, and again esterified by the same method. The total neutral esters were distilled under diminished pressure, when there were usually obtained (i) a small fraction of low b. p., consisting of the original hydroxy-ester, or the unsaturated ester derived from it by dehydration, or a mixture of both, and (ii) a larger fraction of high b. p.

The latter was mixed with concentrated hydrochloric acid (1·5 vols.) and a small quantity of ethyl alcohol, the mixture heated until homogeneous, an equal volume of hydrochloric acid added, and the whole boiled for two hours to expel ethyl alcohol. An equal volume of water was then added, and the boiling continued for a further six hours. The solution was concentrated on a water-bath, and the syrupy residue dissolved in ether. The ethereal solution was thoroughly dried with calcium chloride, and the solvent evaporated, a residue consisting of a pure polybasic acid being thereby obtained.

In certain cases, a portion of the acidic condensation product was esterified, and the neutral ester obtained in this way purified by distillation under diminished pressure. These esterifications proceeded with some difficulty when the crude ester was treated with alcohol and sulphuric acid. Recourse was therefore had to the "benzene" method. The acid esters, dissolved in five times the weight of absolute ethyl alcohol, were heated with a small quantity of zinc chloride, and from time to time the water formed was removed by distillation in a current of benzene vapour. A considerable proportion of the solvent was evaporated, and the solution was poured into water and extracted with ether. In these circumstances, very little acid material was removed from the extract by a solution of sodium carbonate, and the cyano-ester was obtained in the pure condition by distillation. It was hydrolysed in the manner already described in the case of the neutral condensation product.

Attempt to Condense Ethyl Glycollate.

Ethyl glycollate gave no trace of condensation product, the substances isolated being the unchanged ester and glycollic acid.

Condensation of Ethyl Lactate.

Ethyl lactate gave a very poor yield of ethyl α-cyanoglutarate. It was found most convenient to esterify the acidic condensation product, and to add the ester to the neutral product before distilling. Even then the condensation had to be repeated before the less volatile fraction was obtained in a quantity sufficient for purification. The recovered material was mainly unaltered ethyl lactate.

The ethyl α-cyanoglutarate prepared by this method boiled at 138—141°/20 mm. (Found: C=55·6; H=7·2. Calc.: C=56·3; H=7·0 per cent.), and on hydrolysis gave glutaric acid unaccompanied by any other substance.

The glutaric acid was crystallised from benzene (Found: C=45·5; H=6·1. Calc.: C=45·5; H=6·1 per cent.), and identified by comparison with an authentic specimen prepared from *cyclo*-pentanone.

Condensation of Ethyl α-Hydroxyisobutyrate.

This condensation yielded about equal quantities of neutral and acid condensation products.

Ethyl γ-cyano-α-methylglutarate was obtained by distilling the

neutral product as a colourless liquid, which boiled at 160—162°/24 mm. (Found: C=58·4; H=7·5. $C_{11}H_{17}O_4N$ requires C=58·1; H=7·5 per cent.).

Ethyl γ-cyano-α-methylbutyrate, obtained from the distilled, acidic product by washing with a solution of sodium carbonate, boiled at 210—212°/755 mm. (Found: C=61·6; H=8·4. $C_8H_{13}O_2N$ requires C=61·9; H=8·4 per cent.).

Ethyl α-methylglutarate, obtained by hydrolysis and re-esterification of the acidic condensation product, boiled at 238°/atm. (Found, C=59·2; H=8·9. Calc., C=59·4; H=8·9 per cent.).

α-Methylglutaric Acid.—This acid was produced by hydrolysing each of the three esters just mentioned. It was identified by analysis (Found, C=49·35; H=6·9. Calc., C=49·3; H=6·9 per cent.), and by direct comparison with a genuine specimen prepared from α-methylglutaconic acid.

Condensation of Ethyl Hydracrylate.

This condensation gave in good yield about equal weights of neutral and acidic products.

Ethyl α-cyanoglutarate, prepared from the neutral oil by distillation, boiled at 140—145°/21—22 mm. (Found, C=56·15; H=7·0. Calc., C=56·3; H=7·0 per cent.).

Ethyl γ-cyanobutyrate was obtained from the distilled, acidic condensation product. It boiled at 200—202°/755 mm. (Found, C=59·9; H=7·7. Calc., C=59·6; H=7·8 per cent.).

Ethyl glutarate was prepared from the acidic product by hydrolysis and re-esterification; it boiled at 230°. The ester was not analysed, but converted directly into glutaric acid.

Glutaric acid was obtained by the hydrolysis of all three esters, and identified by direct comparison with an authentic specimen (Found, C=45·4; H=6·0. Calc., C=45·5; H=6·1 per cent.).

Condensation of Ethyl β-Hydroxybutyrate.

This substance also condensed easily, and very little unchanged material was recovered.

Ethyl α-cyano-β-methylglutarate, the main constituent of the neutral condensation product, boiled at 180—185°/24 mm. (Found, C=57·85; H=7·6. $C_{11}H_{17}O_4N$ requires C=58·1; H=7·5 per cent.).

Ethyl γ-cyano-β-methylbutyrate was prepared from the distilled, acidic condensation product in the manner already described; it

boiled at 205—209°/atm. (Found, C=61·7; H=8·4. $C_8H_{13}O_2N$ requires C=61·9; H=8·4 per cent.).

Ethyl β-methylglutarate was obtained from the acidic product by hydrolysis and re-esterification. It boiled at 235° (Found, C=59·7; H=9·0. Calc., C=59·4; H=8·9 per cent.).

β-Methylglutaric Acid.—This substance was produced by hydrolysing each of the preceding three esters. It was crystallised from concentrated hydrochloric acid (Found, C=49·45; H=7·0. Calc., C=49·3; H=6·9 per cent.), and identified by direct comparison with a genuine specimen prepared by Day and Thorpe's method (*loc. cit.*).

Condensation of Ethyl α-Hydroxyglutarate.

This ester (this vol., p. 318, footnote) gave only a small yield of condensation product. It was necessary to esterify the acid esters and to add the product to the neutral condensation product in order to obtain the cyano-ester in sufficient quantity to be distilled.

Ethyl ω-cyanomethanetriacetate,

$$CO_2Et{\cdot}CH(CN){\cdot}CH(CH_2{\cdot}CO_2Et)_2,$$

prepared by this method, could not be completely purified owing to lack of material. There was, however, no doubt as to its identity, because on hydrolysis it evolved carbon dioxide and was converted into methanetriacetic acid.

Methanetriacetic acid, when crystallised from dry ether, melted at 113—114°, and was identified by direct comparison with an authentic specimen (Found, C=44·6; H=5·2. Calc., C=44·2; H=5·3 per cent.).

Condensation of Ethyl Malate.

Ethyl malate condensed very readily, only a small quantity of unchanged ester remaining. About equal quantities of neutral and acidic products were formed.

Ethyl α-cyanotricarballylate, prepared by distilling the neutral condensation product, boiled at 190—192°/14 mm. (Found, C=54·75; H=6·7. Calc., C=54·7; H=6·7 per cent.).

Ethyl α-cyanopropane-βγ-dicarboxylate, produced by distilling the acidic condensation product, was purified by washing with a solution of sodium carbonate and by redistillation. It boiled at 166—169°/27 mm. (Found, C=56·5; H=7·1. $C_{10}H_{15}O_4N$ requires C=56·3; H=7·0 per cent.).

Ethyl tricarballylate, obtained from the acidic condensation pro-

duct by hydrolysis and re-esterification, boiled at 200—205°/20 mm. (Found, C=55·7; H=7·8. Calc., C=55·4; H=7·7 per cent.).

Tricarballylic acid was obtained by the hydrolysis of each of the preceding three esters. It was crystallised from acetone (Found, C=40·8; H=4·6. Calc., C=40·9; H=4·5 per cent.) and identified by comparison with a specimen prepared by the reduction of aconitic acid.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [Received, January 26th, 1921.]

XLII.—*Experiments on the Synthesis of the Polyacetic Acids of Methane. Part I. The Conditions Controlling Synthesis by the Cyanoacetic Ester Method, and the Preparation of Methanetriacetic Acid.*

By CHRISTOPHER KELK INGOLD.

THE work described in this paper originated in some experiments which were instituted at the request of Prof. J. F. Thorpe with the object of devising methods suitable for the preparation in quantity of certain polyacetic acids of methane, such as the triacetic acid (I), the carboxytriacetic acid (II), and the tetra-acetic acid (III). These acids are required in connexion with the studies

$$\underset{\text{(I.)}}{CH(CH_2{\cdot}CO_2H)_3} \qquad \underset{\text{(II.)}}{CO_2H{\cdot}C(CH_2{\cdot}CO_2H)_3} \qquad \underset{\text{(III.)}}{C(CH_2{\cdot}CO_2H)_4}$$

with *spiro*- and associated ring compounds which are being carried out in this laboratory, and several methods of synthesis are at present being attempted.

It so happens that all three of these acids are peculiarly difficult to prepare, because the more usual methods of synthesis cannot be applied.

In the preceding paper (p. 329), the question of the mechanism of cyanoacetic ester condensations in general was discussed, and it was shown that the great majority of these were to be referred to the direct addition of ethyl cyanoacetate to an unsaturated compound. They bear, in fact, a close relationship to the synthetic method of Michael, which may be illustrated thus:

$$R_1R_2C{:}CH{\cdot}CO_2Et \longrightarrow R_1R_2C{<}{\begin{matrix}CH_2{\cdot}CO_2Et\\CH(CN){\cdot}CO_2Et\end{matrix}} \longrightarrow R_1R_2C{<}{\begin{matrix}CH_2{\cdot}CO_2H\\CH_2{\cdot}CO_2H\end{matrix}}.$$

In view of this, the difficulty of preparing the higher polyacetic acids of methane by a cyanoacetic ester synthesis will readily be understood, for it will be observed that the unsaturated acids IV, V, and VI, having in their compositions one molecule of acetic acid less than the polyacetic acids I, II, and III, are all substances

$$\underset{\text{(IV.)}}{CO_2H\cdot CH{:}CH\cdot CH_2\cdot CO_2H} \qquad \underset{\text{(V.)}}{CO_2H\cdot CH{:}C(CO_2H)\cdot CH_2\cdot CO_2H}$$

$$\underset{\text{(VI.)}}{CO_2H\cdot CH{:}C(CH_2\cdot CO_2H)_2}$$

of the "mobile"* glutaconic type, that is to say, in their permanent forms they are *not* unsaturated acids. The detailed investigations made during the past few years by Thorpe and his collaborators have revealed many of the peculiarities of such substances. In their "normal" or most permanent forms, they are best represented by symmetrical formulæ of the semi-aromatic

$$\underset{\text{(VII.)}}{CO_2H\cdot\dot{C}H\cdot CH_2\cdot\dot{C}H\cdot CO_2H} \qquad \underset{\text{(VIII.)}}{CO_2H\cdot\dot{C}H\cdot CH(CO_2H)\cdot\dot{C}H\cdot CO_2H}$$

$$\underset{\text{(IX.)}}{CO_2H\cdot\dot{C}H\cdot CH(CH_2\cdot CO_2H)\cdot\dot{C}H\cdot CO_2H}$$

type, such as VII, VIII, and IX. Such substances are not unsaturated, and are exceedingly unreactive. They exist, however, in tautomeric equilibrium with their unstable, unsaturated isomerides. The possibility of obtaining condensation products therefore clearly depends on the relative permanence of the phases and the rapidity of the tautomeric interchange.

The determining conditions are well illustrated by the case of β-methylglutaconic acid, which has been dealt with by Thorpe and Wood (T., 1913, **103**, 1579) and by Thorpe (T., 1919, **115**, 679). Here tautomeric interchange is exceptionally slow, and esters of the unsaturated modification of the acid can be kept in the dark for years without appreciable isomerisation. The unsaturated ester, therefore, when treated with ethyl sodiocyanoacetate, reacts as such, without appreciable conversion into the normal form, and gives a good yield of the expected condensation product.

$$MeC\begin{cases}CH_2\cdot CO_2Et\\ CH\cdot CO_2Et\end{cases} + CHNa(CN)\cdot CO_2Et \longrightarrow MeC\begin{cases}CH_2\cdot CO_2Et\\ CNa(CN)\cdot CO_2Et\\ CH_2\cdot CO_2Et\end{cases}$$

(Good yield.)

* The term "mobile" is used to denote those glutaconic acids which possess the necessary "mobile" hydrogen atom. It will be remembered that glutaconic acids of the type $CO_2H\cdot CR_2\cdot CH{:}CH\cdot CO_2H$ behave normally and readily undergo the condensation reactions of $\alpha\beta$-unsaturated compounds.

Similarly, the normal ester, which, in the presence of a reagent for unsaturated compounds, such as ethyl sodiocyanoacetate, might be expected to undergo slow conversion into the unsaturated form as the equilibrium became disturbed, actually remains quite unaffected so far as any observable tautomeric change is concerned. It appears, however, to have a slight affinity of its own for ethyl sodiocyanoacetate, and, after a long period of heating, there is obtained a small yield of a 1:3-addition product isomeric with that derived from the unsaturated ester:

$$\mathrm{MeCH}{<}\begin{matrix}\dot{\mathrm{C}}\mathrm{H\cdot CO_2Et}\\ \mathrm{CH\cdot CO_2Et}\end{matrix} + \mathrm{CHNa(CN)\cdot CO_2Et} \longrightarrow \mathrm{MeCH}{<}\begin{matrix}\mathrm{CH_2\cdot CO_2Et}\\ \mathrm{CH(CO_2Et)\cdot CNa(CN)\cdot CO_2Et}\end{matrix}$$

(Poor yield.)

In the case of glutaconic ester itself, the tautomeric exchange is sufficiently rapid to render impossible the separate isolation of the two forms. The one ester which can be isolated is essentially of the normal type, although, of course, it must contain the minute trace of the unsaturated isomeride necessary for the establishment of equilibrium. The reaction tending to restore equilibrium when it is disturbed by the removal of the unsaturated ester appears to proceed with a fairly high velocity, and, in spite of the very low concentration of this substance, it is possible to isolate a condensation product evidently derived directly from it. Naturally, however, the yield is very small, and amounts only to a few units per cent., even under the most favourable conditions (*loc. cit.*):

$$\mathrm{CH_2}{<}\begin{matrix}\dot{\mathrm{C}}\mathrm{H\cdot CO_2Et}\\ \mathrm{CH\cdot CO_2Et}\end{matrix} \rightleftarrows \mathrm{CH}{<}\begin{matrix}\mathrm{CH_2\cdot CO_2Et}\\ \mathrm{CH\cdot CO_2Et}\end{matrix} \longrightarrow \mathrm{CH}{\lt}\begin{matrix}\mathrm{CH_2\cdot CO_2Et}\\ \mathrm{CNa(CN)\cdot CO_2Et}\\ \mathrm{CH_2\cdot CO_2Et}\end{matrix}$$

(X.)—(Poor yield.)

When this condensation product (X) is hydrolysed, the *triacetic* acid (I) is obtained, but as a means of preparing this acid for further research the method is clearly impracticable.

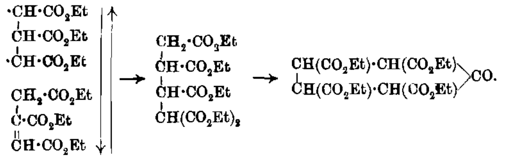
Ethyl aconitate, from which one might expect to obtain the acid (II) by condensation with ethyl cyanoacetate and hydrolysis of the product, is also apparently an equilibrium mixture of the normal and labile (unsaturated) isomerides, but with this important difference: that, owing to the presence of the carbethoxyl group attached *to the central carbon atom, both isomerides yield* the same end-product with the sodium compound of the cyano-ester. The reaction between ethyl aconitate and ethyl sodiocyanoacetate has not previously been investigated, but Auwers and his collaborators (*Ber.*, 1888, **21**, 242; 1891, **24**, 313; 1893, **26**, 366;

1894, **27**, 1121; 1895, **28**, 882) experienced no difficulty in obtaining condensation products with ethyl sodiomalonate. On hydrolysis, they obtained three acids, two of which were modifications of *n*-butane-αβγδ-tetracarboxylic acid (XI), and the third *cyclo*pentanone-3:4-dicarboxylic acid (XII). The condensation

$CH_2(CO_2H){\cdot}CH(CO_2H){\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$ (XI.)

$\begin{matrix} CO_2H{\cdot}CH{\cdot}CH_2 \\ CO_2H{\cdot}CH{\cdot}CH_2 \end{matrix}\!>\!CO$ (XII.)

evidently must have taken the following course, the malonic ester residue having become attached to the α-carbon atom of the aconitic molecule:



Many experiments were made with the object of causing the addition to take place in the reverse direction. In the first place, it was found that the replacement of ethyl malonate by ethyl cyanoacetate, besides effecting an improvement in the yield, greatly simplified the manipulation, as the separation by fractional crystallisation of three very soluble acids, which made Auwers' experiments so laborious, was entirely avoided. There were two condensation products, a normal cyano-ester (XIII) and an acid ester, apparently having the formula XIV. These were easily separated by taking advantage of the solubility of the latter in

$CH_2(CO_2Et){\cdot}CH(CO_2Et){\cdot}CH(CO_2Et){\cdot}CH(CN){\cdot}CO_2Et$ (XIII.)

$\begin{matrix} CH(CO_2Et){\cdot}CH(CO_2Et) \\ CH(CO_2Et){-}CH(CO_2H) \end{matrix}\!>\!C{:}NH$ (XIV.)

sodium carbonate solution. The ester (XIII), on hydrolysis, gave one form only of the acid (XI), whilst the acid ester (XIV) yielded solely the ketonic acid (XII).

It will be observed that whilst one might expect the normal variety of ethyl aconitate to yield, through the occurrence of 1:3-addition, nothing but the ester (XIII) and its internal condensation product (XIV), it is by no means obvious why the unsaturated isomeride should not, to some extent at least, condense

in such a way as to yield a product in which the cyanoacetic residue has become attached to the central carbon atom of the aconitic acid skeleton (XVI, p. 346). Such a condensation product should yield the carboxy-triacetic acid (II) on hydrolysis, and repeated efforts were therefore made to prepare the labile or unsaturated form of aconitic ester. With this object, the elimination of acetic acid from ethyl acetylcitrate (Anschütz and Klingemann, *Ber.*, 1885, **18**, 1983), and the esterification under the mildest possible conditions of labile aconitic acid (Bland and Thorpe, T., 1912, **101**, 1490), were investigated. However, the ester obtained in every case appeared very similar to that prepared by esterifying ordinary aconitic acid. On condensing with ethyl sodiocyanoacetate, a mixture of the same two products, XII and XIII, was invariably obtained.

The condensation of ethyl cyanoacetate with the ester of the acid (VI) has not yet been investigated, as the unsaturated acid itself is still unknown. The preparation of this substance is, however, part of the general scheme of work which is at present being undertaken in these laboratories.

The peculiar conditions which regulate the condensations of ethyl cyanoacetate with these unsaturated substances are still, apparently, the controlling factors when halogen compounds are used. Thus, when chloroform is condensed with ethyl sodiomalonate or ethyl sodiocyanoacetate, the stable product is in each case a derivative of glutaconic acid, which refuses to take up another molecule of the additive reagent (Conrad and Guthzeit, *Ber.*, 1882, **15**, 284; Ruhemann and Browning, T., 1898, **73**, 282). It is true that Coutelle, from the condensation product with malonic ester, obtained the triacetic acid (I), but the amount was very small, and he did not succeed in purifying it (*J. pr. Chem.*, 1906, [ii], **73**, 49).

The corresponding condensation, in which chloroform is replaced by carbon tetrachloride, has been studied by several investigators (Chabrié, *Bull. Soc. chim.*, 1892, [iii], **7**, 19; Zelinsky, *Ber.*, 1895, **28**, 2964; Bishoff and Walden, *Ber.*, 1894, **27**, 1493), but no one appears to have succeeded in isolating even a trace of the tetra-acetic acid (III).

The condensation of ethyl sodiocyanoacetate with ethyl β-chlorotricarballylate might be expected to yield a product (see next page) which on hydrolysis should give the carboxytriacetic acid (II). Here again, however, the tendency to form a substance of the glutaconic type is so great that no trace of the expected condensation product is obtained, the whole of the chloro-ester being apparently first converted into ethyl aconitate, which then yields a mixture of

the two esters, XIII and XIV, in the way already described. Examples of this type of reaction between ethyl cyanoacetate and halogen compounds are certainly very rare.

$$\begin{array}{l}CH_2\cdot CO_2Et\\ |\\ CCl\cdot CO_2Et\\ |\\ CH_2\cdot CO_2Et\end{array} + CHNa(CN)\cdot CO_2Et \longrightarrow$$

$$\begin{array}{l}CH_2\cdot CO_2Et\\ |\\ C(CO_2Et)\cdot CNa(CN)\cdot CO_2Et\\ |\\ CH_2\cdot CO_2Et\end{array} \longrightarrow \begin{array}{l}CH_2\cdot CO_2H\\ |\\ C(CO_2H)\cdot CH_2\cdot CO_2H\\ |\\ CH_2\cdot CO_2H\end{array}.$$

The more obvious synthetical methods having, for reasons already noticed, failed to produce the desired substances, it became necessary to devise others. In the preceding paper (this vol., p. 329), it has been shown that ethyl sodiocyanoacetate enters into condensation with the esters of hydroxy-acids, and that in some cases the reaction proceeds with great readiness. It was hoped, therefore, that ethyl β-hydroxyglutarate would yield a condensation product (XV) which, on hydrolysis, should give the triacetic acid (I), whilst ethyl citrate should in a similar way give rise ultimately to the carboxytriacetic acid (II). The method appeared particularly attractive, on account of the availability of the starting materials:

$$\begin{array}{l}CH_2\cdot CO_2Et\\ |\\ CH\cdot OH\\ |\\ CH_2\cdot CO_2Et\end{array} \longrightarrow \begin{array}{l}CH_2\cdot CO_2Et\\ |\\ CH\cdot CH(CN)\cdot CO_2Et\\ |\\ CH_2\cdot CO_2Et\\ \quad (XV.)\end{array} \longrightarrow \begin{array}{l}CH_2\cdot CO_2H\\ |\\ CH\cdot CH_2\cdot CO_2H\\ |\\ CH_2\cdot CO_2H\end{array} \quad (I.)$$

$$\begin{array}{l}CH_2\cdot CO_2Et\\ |\\ C(OH)\cdot CO_2Et\\ |\\ CH_2\cdot CO_2Et\end{array} \longrightarrow \begin{array}{l}CH_2\cdot CO_2Et\\ |\\ C(CO_2Et)\cdot CH(CN)\cdot CO_2Et\\ |\\ CH_2\cdot CO_2Et\\ \quad XVI.)\end{array} \longrightarrow$$

$$\begin{array}{l}CH_2\cdot CO_2H\\ |\\ C(CO_2H)\cdot CH_2\cdot CO_2H\\ |\\ CH_2\cdot CO_2H\end{array} \quad (II.)$$

Experiment fully justified the first of these suppositions, but not the second. Ethyl β-hydroxyglutarate, on condensation and hydrolysis, gave a yield of methanetriacetic acid (I) amounting to 60 per cent. of the theoretical, calculated on the hydroxy-ester employed. Ethyl citrate, on the other hand, gave a mixture of condensation products, which, on hydrolysis, yielded the two acids

(XI and XII) that had previously been obtained from ethyl aconitate. No trace of the polyacetic acid (II) could be isolated.

Broadly speaking, these results are in agreement with the view expressed in the former paper (*loc. cit.*), that all such condensations proceed by way of an unsaturated, intermediate product. The remarkably high yield of the condensation product obtained from β-hydroxyglutaric ester requires special notice, however, as, in view of the course followed by the other condensations with hydroxy-esters (*loc. cit.*), there appears in this case to be operating some condition which requires elucidation. This matter will be dealt with in another paper.

There is therefore no longer any difficulty in preparing methanetriacetic acid (I) in large quantities. Acetonedicarboxylic acid is first prepared by treating citric acid with fuming sulphuric acid, as described by von Pechmann (*Annalen*, 1891, **261**, 155), and then reduced with sodium amalgam to β-hydroxyglutaric acid (Blaise, *Bull. Soc. chim.*, 1903, [iii], **29**, 1012). This is then esterified, and treated as described in the experimental part of this paper.

The two remaining polyacetic acids, as well as the unsaturated derivative (VI, p. 342), have so far evaded all attempts at their preparation, but several series of experiments are still in progress, with every hope of ultimate success.

EXPERIMENTAL.

(a) *Condensation of Ethyl Aconitate with Ethyl Cyanoacetate.*

Ethyl aconitate (258 grams) was added to a suspension in 300 grams of ethyl alcohol, of ethyl sodiocyanoacetate prepared from 23 grams of sodium, and 113 grams of the cyano-ester. There was an immediate rise of temperature, and the sodium compound dissolved, forming a deep yellow solution. This was heated on the steam-bath for seven hours, and the product was then poured into 2·5 litres of water and extracted with ether (neutral extract). The aqueous liquid was acidified with hydrochloric acid, and again extracted with ether, the extract being subsequently washed with a dilute solution of sodium carbonate (quasi-acid extract). The alkaline washings were acidified and again extracted (acid extract). The first two extracts were well washed with water to remove any dissolved alcohol. The residue obtained after drying and evaporating the first extract weighed 70 grams, that from the second extract 120 grams, and from the third 140 grams.

The residue from the quasi-acid extract was an individual substance, *b. p.* 230°/11 mm. About 40 grams of unchanged ethyl aconitate were obtained by distillation of the neutral fraction;

the remainder partly decomposed, but 18 grams of distillate were collected, nearly the whole of which was found to be identical with the substance forming the quasi-acid fraction.

*Ethyl α-Cyano-*n*-butane-αβγδ-tetracarboxylate* (XIII, p. 344).

The distillate, b. p. 230°/11 mm., consists of this cyano-ester in the pure condition. It is a colourless, viscous oil (Found: C=54·8; H=6·8. $C_{17}H_{25}O_8N$ requires C=55·0; H=6·7 per cent.).

n-*Butane-αβγδ-tetracarboxylic Acid* (XI, p. 344).

A mixture of the cyano-tetracarboxylic ester and an equal volume of cold concentrated sulphuric acid was diluted after twelve hours with sufficient water to cause a slight precipitation of oil, and then heated for four hours on the sand-bath. During the first two hours' heating, carbon dioxide was evolved copiously, and there was one stage at which care had to be taken to avoid loss by frothing. The solution was cooled, saturated with ammonium sulphate, and extracted with ether. The mixture of acids obtained from the extract appeared to contain traces of acid esters, and was therefore dissolved in ten times its weight of concentrated hydrochloric acid and boiled for six hours to expel ethyl alcohol. The residual solution was decolorised with charcoal, evaporated on a water-bath, and the residue dissolved in ether. The extract was dried with calcium chloride, filtered, and evaporated. *n*-Butane-αβγδ-tetracarboxylic acid was thus obtained as a white residue, which was crystallised from water (Found: C=41·15; H=4·3. Calc.: C=41·0; C=4·3 per cent.). It melted at 189°, steam being evolved and the anhydro-acid formed.

The *anhydro-acid*, m. p. 232°, was readily obtained by heating the preceding acid at 200° for a few minutes (Found: C=44·2; H=3·8. Calc.: C=44·4; H=3·7 per cent.).

Ethyl n-*Butane-αβγδ-tetracarboxylate*, $\underset{CO_2Et}{CH_2}-\underset{CO_2Et}{CH}-\underset{CO_2Et}{CH}-\underset{CO_2Et}{CH_2}$.

In view of the decomposition which ensued when the residue from the neutral extract was distilled, the same material, obtained in another experiment, was distilled under reduced pressure until the whole of the ethyl aconitate had passed over, and the residue was then hydrolysed completely by successive treatment with sulphuric acid and hydrochloric acid, as already described for the hydrolysis of the α-cyanotetracarboxylic ester. The acid so obtained melted indefinitely at 165—180°, and was therefore

sterified with alcohol and sulphuric acid. The esters were isolated y extraction with ether in the usual way, and the acid esters emoved by washing the extract with a solution of sodium carbon-te. These were re-extracted from the washings after acidifying, nd again esterified by the same method. This process was repeated third time, when only a negligible amount of acid material emained. The combined neutral esters, when distilled under iminished pressure, were easily separated into two fractions differ-ng widely in boiling point. The less volatile fraction, after edistillation, boiled at 201°/13 mm., and was found to consist f *ethyl* n-*butane-αβγδ-tetracarboxylate* (Found: C = 55·6; H = 7·6. $C_{16}H_{26}O_8$ requires C = 55·5; H = 7·5 per cent.).

The constitution of this ester was proved by hydrolysis. It was iixed with 1·5 times its volume of concentrated hydrochloric acid nd a little ethyl alcohol. The mixture was shaken until emulsi-cation was fairly permanent, heated until a clear solution was btained, and then boiled for six hours in such a way that alcohol apour could escape freely, fresh hydrochloric acid being added rom time to time to prevent the solution becoming too concen-rated. Finally, the solution was evaporated on a water-bath, hen *n*-butane-αβγδ-tetracarboxylic acid crystallised.

Ethyl cyclo*Pentanone*-3 : 4-*dicarboxylate*, $\begin{matrix} CO_2Et\cdot CH\cdot CH_2 \\ CO_2Et\cdot CH\cdot CH_2 \end{matrix}\!\!>CO$.

The more volatile fraction from which the above tetracarboxylic ster was separated by distillation yielded, when redistilled, a olourless, mobile liquid, which boiled at 160—162°/15 mm. This roved to be *ethyl* cyclo*pentanonedicarboxylate* (Found: C = 58·1; I = 6·9. $C_{11}H_{16}O_5$ requires C = 57·9; H = 7·0 per cent.).

cyclo*Pentanone*-3 : 4-*dicarboxylic Acid*.

This acid may be obtained by hydrolysing its ester with hydro-hloric acid. The hydrolysis was conducted in the same manner s that of ethyl *n*-butane-αβγδ-tetracarboxylate. In this case, owever, some darkening of colour occurred, and the concentrated olution was therefore extracted with ether. The residue from the ther was only slightly coloured, and, after crystallisation from a iixture of acetone and benzene, melted at 189° without decom-osition.

The same acid was the sole product when the residue from the riginal acid extract was completely hydrolysed. It was mixed ith an equal volume of concentrated sulphuric acid, and, after

some hours, with twice this volume of water. The solution was heated to complete the elimination of carbon dioxide, then diluted, and boiled under a short air condenser for five hours. After saturating the solution with ammonium sulphate, the organic acids were extracted by means of ether. The residue (m. p. 181—186°) remaining after evaporation of the ether yielded *cyclo*pentanone-3:4-dicarboxylic acid (m. p. 189°) after two or three recrystallisations from water. Owing, however, to the very soluble character of the acid, it was found best to esterify the crude acid with ethyl alcohol and sulphuric acid, and to hydrolyse the ester, after distillation, by means of hydrochloric acid, as already described (Found: C=48·6; H=4·6. Calc.: C=48·8; H=4·7 per cent.).

*cyclo*Pentanone-3:4-dicarboxylic acid has already been prepared by Auwers (*loc. cit.*), but does not appear to have been characterised by any crystalline derivatives.

The *semicarbazone* separated readily when an aqueous solution of the acid was mixed with one of semicarbazide acetate. It was obtained by crystallisation from glacial acetic acid in long needles melting and decomposing at 225° (Found: C=42·1; H=4·8. $C_8H_{11}O_5N_3$ requires C=41·9; H=4·8 per cent.).

The *dianilide* was prepared in the usual manner. It crystallised from alcohol in needles, which melted, with decomposition, at 195° (Found: C=70·4; H=5·35. $C_{19}H_{18}O_3N_2$ requires C=70·8; H=5·6 per cent.).

(b) *The Preparation of Ethyl Aconitate.*

(i) *From Normal Aconitic Acid.*—The condensations just described were carried out with ethyl aconitate, which had been prepared by esterifying normal aconitic acid (m. p. 191°) by means of ethyl alcohol and sulphuric acid.

(ii) *From Ethyl Acetylcitrate.*—A similar series of experiments were made with a specimen of ethyl aconitate, which had been prepared by the elimination of acetic acid from ethyl acetylcitrate (Anschütz and Klingemann, *loc. cit.*). The results, however, were the same as those just described.

(iii) *From "Labile" Aconitic Acid.*—A third series of experiments were carried out, using a specimen of ester which had been made from Bland and Thorpe's "labile" aconitic acid (*loc. cit.*) by esterification with ethyl alcohol in the presence of a small quantity of zinc chloride. This ester (Found: C=55·55; H=7·1. Calc.: C=55·8; H=7·0 per cent.) appeared very similar to the

others, and gave the same series of condensation products when treated with ethyl sodiocyanoacetate.

(iv) *From the "Labile" Silver Salt.*—Finally, in order to eliminate as far as possible all opportunity for isomerisation to the normal form, "labile" aconitic acid (m. p. 173°) was first converted into its *silver* salt (Found: Ag = 65·3. $C_6H_3O_6Ag_3$ requires Ag = 65·5 per cent.), and thence into its ethyl ester by the action of ethyl iodide. The ester (Found: C = 55·8; H = 6·95. Calc.: C = 55·8; H = 7·0 per cent.) prepared by this method, however, *appeared to react with ethyl sodiocyanoacetate just as in* the former cases.

(c) *Condensation of Ethyl β-Chlorotricarballylate with Ethyl Sodiocyanoacetate.*

Bertram was unable to isolate any of the products of this condensation (*Ber.*, 1903, **36**, 3297).

The chloro-ester (290 grams) was mixed with a suspension in 300 grams of ethyl alcohol of ethyl sodiocyanoacetate, prepared from 113 grams of the ester and 23 grams of sodium. The mixture, after being heated for thirty-six hours on the steam-bath, was poured into dilute hydrochloric acid, and the esters extracted with ether. On washing the extract with a solution of sodium carbonate, a large part of the material passed into the aqueous layer, from which it was recovered by re-extraction after acidification.

The residue from the neutral extract weighed 110 grams. The greater part distilled at about 170°/12 mm., and consisted essentially of ethyl aconitate. Besides this, however, 13 grams of an ester boiling at 230—232°/12 mm. were obtained. This proved to be ethyl α-cyano-*n*-butane-αβγδ-tetracarboxylate (Found: C = 55·3; H = 6·9. Calc.: C = 55·0; H = 6·7 per cent.). On hydrolysis, it gave *n*-butane-αβγδ-tetracarboxylic acid, but no trace of any isomeride.

The residue from the acid extract weighed about 200 grams, and was hydrolysed in exactly the same way as the residue from the acid extract of the condensation product with ethyl aconitate (p. 349). The crude product of hydrolysis was purified by distilling its ethyl ester (see p. 349). The distilled ester, when again hydrolysed by hydrochloric acid, gave pure *cyclo*pentanone-3:4-dicarboxylic acid (Found: C = 48·4; H = 4·4. Calc.: C = 48·8; H = 4·7 per cent.).

(d) *Condensation of Ethyl β-Hydroxyglutarate with Ethyl Sodiocyanoacetate.*

This condensation was effected by the general method given in the experimental part of the preceding paper (this vol., p. 329), the acid condensation product being esterified with ethyl alcohol, and the ester added to the neutral product before purifying by distillation.

Ethyl ω-Cyanomethanetriacetate (XV, p. 346).

The cyano-ester distilled almost entirely at 203—204°/13 mm. as a colourless liquid (Found: C=56·1; H=7·1. $C_{14}H_{21}O_6N$ requires C=56·2; H=7·0 per cent.). The yield was 65 per cent. of the theoretical.

Methanetriacetic Acid (I, p. 341).

The cyano-ester was hydrolysed by means of dilute sulphuric acid, the method being that given in the former paper (*loc. cit.*) for the hydrolysis of neutral condensation products. The ethereal extract of the acid left, on evaporation, a straw-coloured syrup, which, by contact with a rod, suddenly solidified with a considerable evolution of heat. The yield of crude product, which melted at 111—114°, amounted to 93 per cent. of the theoretical. After crystallisation from ether, the acid melted at 115° (Found: C=44·2; H=5·3. Calc.: C=44·2; H=5·3 per cent.).

When this acid was first prepared, there was some doubt as to whether it might not be *n*-butane-αβδ-tricarboxylic acid, which might conceivably have been formed under the experimental conditions employed, and is isomeric with the substance actually obtained. *n*-Butane-αβδ-tricarboxylic acid has been described as melting at 116—118°, and, although it has been prepared by several investigators (Auwers, Köbner, and Mayenburg, *Ber.*, 1891, **24**, 2895; Guthzeit and Engelmann, *J. pr. Chem.*, 1902, [ii], **66**, 104; Silberrad, T., 1904, **85**, 612; Kay and Perkin, T., 1906, **89**, 1644; Howarth and Perkin, T., 1908, **93**, 575; Leuchs and Möbis, *Ber.*, 1909, **42**, 1232), does not appear to have been characterised by any crystalline derivative. On the other hand, methanetriacetic acid has not previously been obtained in sufficient quantity to enable a derivative to be prepared. In order to settle the point, *n*-butane-αβδ-tricarboxylic acid was prepared from ethyl sodioethanetricarboxylate and ethyl β-iodopropionate (Kay and Perkin, *loc. cit.*), and directly compared with the acid obtained from ethyl β-hydroxyglutarate. They were found to differ in

crystalline form, in their solubility in ether, the former being the less soluble, and in their tendency to crystallise from mixtures of solvents. Further, a mixture of the two acids melted at 80—90°.

The *anhydro-acid*, $CO_2H\cdot CH_2\cdot CH<\begin{smallmatrix}CH_2\cdot CO\\CH_2\cdot CO\end{smallmatrix}>O$, was prepared by digesting the acid (m. p. 115°) with acetyl chloride. On evaporating the acetic acid and excess of acetyl chloride, the anhydro-acid was obtained as a viscous, colourless gum (Found: C=48·5; H=4·8. $C_7H_8O_5$ requires C=48·8; H=4·6 per cent.).

The *dianilic acid*, $CO_2H\cdot CH_2\cdot CH(CH_2\cdot CO\cdot NH\cdot C_6H_5)_2$, was produced by digesting the acid with thionyl chloride (2·5 mols.), and, after removing the volatile products by warming at 80° under reduced pressure, adding an excess of aniline. The horn-like product was triturated with dilute hydrochloric acid and boiled with water until sufficiently granular to filter, and then washed with a dilute solution of sodium carbonate to separate the anilic acid from the amorphous, neutral products. The dianilic acid, precipitated in crystalline form by acidifying the washings, was recrystallised from glacial acetic acid, and obtained in prismatic needles melting at 192° (Found: C=66·9; H=6·1. $C_{19}H_{20}O_4N_2$ requires C=67·1; H=5·9 per cent.).

(e) *Condensation of Ethyl Citrate with Ethyl Sodiocyanoacetate.*

This condensation was effected by the method already indicated (this vol., p. 336). On extracting the product, most of it dissolved in the acid extract.

The neutral extract, which contained a bright green impurity, gave, on distillation, besides unchanged ethyl citrate, a small quantity of ethyl α-cyano-*n*-butanetetracarboxylate (Found: C=55·3; H=6·6. Calc.: C=55·0; H=6·7 per cent.). The constitution of this ester was proved by hydrolysis with dilute sulphuric acid, when the sole product was *n*-butane-αβγδ-tetracarboxylic acid.

The acid extract was evaporated, and the residue hydrolysed in the same manner as the acid product derived from ethyl aconitate (p. 349). The crude product of hydrolysis readily solidified when the ethereal extract was evaporated, but, as it did not melt quite sharply, it was esterified by means of ethyl alcohol and sulphuric acid. Practically all the ester so obtained boiled at 155—158°/13 mm., and, when thus purified, yielded pure *cyclo*pentanone-3:4-dicarboxylic acid on hydrolysis with hydrochloric acid. The acid was recrystallised from water (Found: C=48·6; H=4·8. Calc.: C=48·8; H=4·7 per cent.).

A substance of high boiling point was also obtained, but in quantity too small for redistillation. It appeared to consist of ethyl *n*-butane-$\alpha\beta\gamma\delta$-tetracarboxylate, as, on hydrolysis with hydrochloric acid, it gave *n*-butane-$\alpha\beta\gamma\delta$-tetracarboxylic acid.

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XLIII.—*The Halogen Derivatives of Nitroform.*

By ALEXANDER KILLEN MACBETH and DAVID DOIG PRATT.

BASCHIERI (*Atti R. Accad. Lincei*, 1901, [v], **9**, i, 392) pointed out that acetylene, when acted upon by nitric acid, yielded nitroform and other products. Orton and McKie (T., 1920, **117**, 283) found that the reaction could best be carried out by passing dry acetylene into anhydrous or 95 per cent. nitric acid, containing mercuric nitrate as a catalyst. Under these conditions the maximum yield of nitroform was obtained, and the formation of secondary products was almost eliminated.

It seemed probable that the halogen derivatives of nitroform might be conveniently prepared by the addition of halogens, or halogen acids, to the nitroform–nitric acid solution obtained by the action of acetylene, and the results of such experiments are now described.

Chlorotrinitromethane.—On passing a stream of dry acetylene through fuming nitric acid (D 1·545) containing 0·5—1·0 per cent. of mercuric nitrate as a catalyst, it was found that absorption was almost complete when the acetylene was passed at the rate of 300—400 c.c. per hour, and the acid was maintained at about 30°. After the reaction had proceeded for over eight hours, oxidation became marked, and little was gained by the further passage of acetylene. In some cases when acetylene had been passed slowly into the acid, and the process continued the next day—the mixture having stood overnight—good yields of nitroform were obtained, judged by the amounts of the chloro-derivative which were subsequently isolated.

Chlorotrinitromethane separates as a heavy oil on the addition of concentrated hydrochloric acid to the nitroform–nitric acid solution obtained by the treatment just described. Under such conditions it is rather impure, containing dissolved nitrous fumes. A better product is secured by diluting the nitric acid mixture before

the addition of hydrochloric acid, but if the dilution is too great it is necessary to heat the mixture under a reflux condenser before the separation of the oil takes place. The heavy oil so obtained is drawn off, washed several times with water, and finally dried over calcium chloride. The average yield from 100 c.c. of nitric acid is 21—25 grams.

The oil distils under ordinary pressures at 133—135°, but a small fraction passes over at 122°. Some decomposition takes place, and in one experiment this was somewhat violent, quantities of nitrous fumes being evolved. Fractional distillation under reduced pressure is therefore advisable, and the introduction of some silver carbonate leads to the separation of a purer product. The oil consists almost entirely of chlorotrinitromethane, as it distils in a main fraction of steady boiling point * (Found: Cl = 19·03, 19·19. CO_6N_3Cl requires Cl = 19·14 per cent.).

Pure chlorotrinitromethane is a clear, mobile oil, with a faint yellow tinge. It boils sharply at 35°/9 mm., 51·5—52°/30 mm. On freezing it is converted into a white, crystalline solid melting at 4·2—4·4°. The refractive index, n_D, is 1·4560, and the density at 19° 1·6616. The oil is soluble in alcohol, ether, and most organic solvents, but is insoluble in water. It has a penetrating, unpleasant odour, somewhat resembling that of chloropicrin, and it affects the eyes. It distils in steam with little decomposition, but is slowly broken down by aqueous and alcoholic solutions of alkali, potassium hydroxide, for example, producing a potassium salt of nitroform according to the equation:

$$3(NO_2)_3CCl + 6KOH = 3(NO_2)_3CK + 2KCl + KClO_3 + 3H_2O.$$

Silver nitrite seems to be without action on chlorotrinitromethane, as no traces of tetranitromethane could be detected even after refluxing for several hours.

Chlorotrinitromethane is also formed by the passage of chlorine into the nitroform–nitric acid solution obtained from acetylene. It may also be prepared by the action of chlorine on aqueous solutions of the potassium salt of nitroform. In one experiment 25 grams of this salt gave more than 20 grams of the crude oil. It cannot be produced directly from tetranitromethane, as aqua regia is without action on the latter, even when the mixture is heated for several hours on the water-bath under a reflux condenser.

Bromotrinitromethane, sometimes inaccurately referred to as

* The chlorine content may be estimated by either the Carius or the Stepanow method (*Ber.*, 1906, **39**, 4056). In the latter case it was found advisable to distil in steam after treatment with sodium and acidifying with nitric acid, in order to remove alcohol and traces of nitroform.

bromopicrin, may easily be obtained by any of the methods employed in the preparation of the chloro-compound. Thus it separates as a dark brown oil when hydrobromic acid or bromine is added to nitroform–nitric acid solutions. When the halogen itself is employed the product is much more impure than when hydrobromic acid is used, containing bromine in considerable amounts. Dilution of the nitric acid is desirable before the addition of the hydrobromic acid, as a purer product is then obtained. After washing the crude oil with water and drying with fused sodium sulphate, bromotrinitromethane is obtained as a pale yellow, heavy liquid. It distils under ordinary pressure, but much decomposition takes place, and the distillate is so deeply coloured as closely to resemble bromine.

Bromotrinitromethane boils at 59°/8 mm., 63°/14 mm., 68°/20 mm., and 78°/33 mm. It is a clear liquid, with a faint greenish-yellow tinge. On cooling, it solidifies to a white, crystalline solid melting at 9·5—10°. The refractive index, n_D, is 1·4900, and the density at 19° 2·07. The smell resembles that of the chloro-compound, but is sharper and less penetrating.

Bromotrinitromethane has previously been described by Schischkow (*Annalen*, 1861, **119**, 247), who prepared it by the action of bromine on nitroform in sunlight. The substance so produced melts under 12°, and has a density of 2·8. No fractional distillation under reduced pressure is recorded. From our observations it would appear that the density previously recorded is too high, as our value is the result of several observations with material from different preparations, and we were able to work with quantities of 15—20 grams.

As the values obtained for the bromine content of our bromotrinitromethane were consistently too high (Found: Br = 38·9. CO_6N_3Br requires Br = 34·8 per cent.), it seemed that it contained traces of some more highly brominated compound.

Rigorous fractional distillation over silver carbonate at reduced pressure and repeated freezing out failed to reduce appreciably the percentage of bromine. This may perhaps best be accounted for by the presence of small amounts of dibromodinitromethane, or other more highly brominated derivative, which does not differ sufficiently in boiling point to be removable by distillation. In support of this view it may be mentioned that the molecular-weight determination (by the freezing-point method in benzene) gave results somewhat too high (average value, 235; theoretical, 230). That the almost entire part of the product consists of bromotrinitromethane is shown by its action with an aqueous or alcoholic solution of potassium hydroxide, which readily converts it into the

potassium salt of nitroform (Found: K = 20·4, 20·47. CO_6N_3K requires K = 20·64 per cent.) according to the equation:

$$3(NO_2)_3CBr + 6KOH = 3(NO_2)_3CK + 2KBr + KBrO_3 + 3H_2O.$$

Bromotrinitromethane distils in steam with little decomposition. It is not converted into tetranitromethane by the action of silver nitrite, even after refluxing for several hours. Attempts to act upon it with magnesium turnings in the hope of preparing a Grignard reagent or hexanitroethane failed, the magnesium being unattacked even after long-continued refluxing in the presence of catalysts. The bromo-compound was recovered unchanged from the reaction mixture.

Iodotrinitromethane, sometimes anomalously referred to as iodopicrin, cannot be prepared by any of the methods outlined above. The addition of hydriodic acid, or iodine, to nitroform–nitric acid solution resulted in the separation of iodic acid and mercuric iodide without the formation of any iodonitro-compound. Unsuccessful attempts to prepare it by refluxing the chloro- and the bromo-analogues with methyl iodide were also made. The action of an alcoholic solution of potassium iodide on the chloro- and bromo-compounds liberated large quantities of iodine and gave solutions which severely attacked the eyes, indicating that some of the iodo-compound was present; attempts to separate it from the mixture, however, were unsuccessful. Meisenheimer and Schwarz (*Ber.*, 1906, **39**, 2543) describe the preparation of iodotrinitromethane by the action of an ethereal solution of iodine on the silver salt of nitroform. The compound is stated to melt at 55—56° with decomposition, and to distil with some decomposition at 48°/13 mm. The latter observation seems doubtful when the boiling points of the chloro- and bromo-compounds are considered, as it is to be expected that the iodo-compound would boil at a higher temperature than the bromo-analogue (63°/14 mm.). It is, moreover, very remarkable to have a substance boiling under reduced pressure at a temperature lower than its melting point, the more especially as a thermodynamical consideration shows that the melting point of a substance is altered by some 0·008° by a change in pressure of one atmosphere. In this connexion it is interesting to note that nitroform, prepared during the course of the present work, was found to distil as a clear, pale yellow liquid at 48°/17 mm., refractive index, $n_D = 1{\cdot}4280$. It therefore appears probable that the iodotrinitromethane decomposed at some stage of Meisenheimer's work with the formation of nitroform.

Colours Produced by Chloro- and Bromo-trinitromethane.—On account of the observations previously recorded in the case of tetra-

nitromethane (Clarke, Macbeth, and Stewart, P., 1913, **29**, 161; Harper and Macbeth, *ibid.*, 1915, **31**, 263; Harper and Macbeth, T., 1915, **107**, 87) it seemed of interest to examine the effect of these substances on compounds containing unsaturated linkings or atoms capable of exercising a higher valency. It is found that colours are produced by these halogen derivatives somewhat similar to those obtained with tetranitromethane. Typical results may best be given in tabular form. In all cases alcoholic solutions of the influencing substances of approximately equal strength were used and three drops of the reagent added to 5 c.c. of the solutions.

Influencing substance.	Colour developed with		
	$(NO_2)_3CCl$.	$(NO_2)_3CBr$.	$(NO_2)_3C\cdot NO_2$.
Ethyl mercaptan ...	Lemon-yellow.	Lemon-yellow.	Yellow, becoming reddish-orange.
Ethyl sulphide ...	Yellow, slowly becoming orange-pink.	Yellow, quickly becoming orange-pink, with evolution of a gas.	Lemon-yellow, becoming pinkish-orange. Not so pronounced as in the case of the bromo-compound.
Carvene	Pale yellow	Pale yellow.	Deep yellow.
Piperidine	Brownish-orange.	Brownish-orange.	Brownish-orange.
Dimethylaniline ...	Dark brown, reddish by transmitted light.	Yellowish-brown.	Blackish-brown, green by transmitted light.

It will be seen from the table that the colours developed by the different substances do not follow any fixed order for the three nitro-compounds. A further spectroscopic study of these new cases may throw further light on the question of the colour production noted in the case of the nitroparaffins, and it is hoped to undertake this work shortly.

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[*Received, January 26th*, 1921.]

XLIV.—*Quantitative Reduction by Hydriodic Acid of Halogenated Malonyl Derivatives. Part I. The Amides and* s.-*Di-alkyl- and- aryl-substituted Amides of Mono- and Di-bromomalonic Acid.*

By John Valentine Backes, Ralph Winton West, and Martha Annie Whiteley.

It was observed by one of us (Whiteley, P., 1908, **24**, 288) that the bromine in the bromomethylene complex of certain mono- and di-bromomalonyl derivatives, $\cdot CO\cdot CHBr\cdot CO\cdot$ and $\cdot CO\cdot CBr_2\cdot CO\cdot$, is reactive towards hydriodic acid in the same sense as the halogen in the nitrogen–halogen complex; such compounds liberate iodine from hydriodic acid at the ordinary temperature according to the following equations:

(I.) $\cdot CO\cdot CHBr\cdot CO\cdot + 2HI = \cdot CO\cdot CH_2\cdot CO\cdot + HBr + I_2$.

(II.) $\cdot CO\cdot CBr_2\cdot CO\cdot + 4HI = \cdot CO\cdot CH_2\cdot CO\cdot + 2HBr + 2I_2$.

Compare $C_6H_5\cdot NCl\cdot CO\cdot CH_3 + 2HI = C_6H_5\cdot NH\cdot CO\cdot CH_3 + HCl + I_2$.

The reaction is complete and can be employed as a method for estimating the bromine in the compound.

The investigation has been extended to include the amides, and typical alkyl- and aryl-substituted amides and ureides of mono- and of di-bromomalonic acid. The melting points of these compounds are tabulated below.

Melting Points of Amides and Substituted Amides and Ureides of Malonic, Bromomalonic, and Dibromomalonic Acids.

Nature of amide	Malonic acid.	Bromo-malonic acid.	Dibromo-malonic acid.
Amide	*170°*	181°	*203°*
s.-Dimethylamide	*135*	164	*161*
s.-Diethylamide	*149*	160	78
s.-Di-*n*-propylamide	139	134·5	78·5
s.-Di-*n*-butylamide	132·5	103	—
s.-Di-*iso*butylamide	126·5	151	100
s.-Dibenzylamide	142	167	128
s.-Diurethane	*124*	148	—
Mono-*p*-bromophenylamide	—	200	142
Mono-2 : 4-dibromophenylamide	194	—	174
Anilide	*225*	—	147
p-Bromoanilide	*268*	236	164
2 : 4-Dibromoanilide	*233*	—	146
2 : 4 : 6-Tribromoanilide	*331*	—	174
4-Bromo-*o*-toluidide	216	233	138
p-Toluidide	*250*	*211*	*137*
2-Bromo-*p*-toluidide	180	—	150
Ureide	*253*	—	*234*
Diphenylureide	*238*	155	*164*
Diphenylthioureide	*244*	*220*	*190*

Note.—The melting points in italics are those of compounds that have been described previously.

All these compounds are quantitatively reduced by hydriodic acid at the ordinary temperature to the corresponding derivative of malonic acid, according to equation (I) or (II). The reduction is carried out by adding solid potassium iodide to a solution of the bromo-compound in glacial acetic acid; at temperatures above 60° the reaction is instantaneous, but requires about two hours at the ordinary temperature.

Kurt Meyer (*Annalen*, 1911, **380**, 212) has made use of the quantitative reduction by hydriodic acid of certain bromo-ketones to estimate the bromo-ketone formed by the bromination of the enolic isomeride present in ordinary ethyl acetoacetate and similar compounds:

$$\cdot C(OH){:}CH\cdot \xrightarrow{Br_2} \cdot CBr(OH)\cdot CHBr\cdot \longrightarrow \cdot CO\cdot CHBr\cdot + HBr.$$

Meyer's method of effecting the reduction was different from that employed by us. The hydriodic acid was generated by the action of concentrated hydrochloric acid on potassium iodide in an alcoholic solution of the bromo-ketone, and the mixture was heated; under these conditions Meyer states that the reaction is a general one for bromo-ketones.

We have examined the behaviour of certain typical bromo-ketones towards the reducing action of hydriodic acid under the two conditions, and find that whilst ω-bromoacetophenone, α-bromo-α-nitrocamphor, and the α-bromo-complex in phenyl αβ-dibromo-β-phenylethyl ketone are quantitatively reduced under each set of conditions, bromoacetone is reduced under Meyer's conditions but not under ours, and α-bromocamphor does not suffer reduction under either set of conditions.

Meyer's explanation of the course of the reducing action of hydriodic acid on bromo-ketones is that it is due to the spontaneous breaking down, with liberation of iodine, of an unstable, intermediate di-iodo-compound, formed by the addition of a molecule of hydrogen iodide to the carbonyl group of the bromo-ketone, and the replacement by iodine of the bromine of the bromomethylene group by reaction with a second molecule of hydrogen iodide:

$$\cdot CO\cdot CBr{:} \longrightarrow \cdot CI(OH)\cdot CI{:} \longrightarrow \cdot C(OH){:}C{:} + I_2.$$

The results we have obtained up to the present, whilst affording no wholly satisfactory explanation of the course of the reaction, give ground for believing that it involves hydrolysis of the bromo-compound with liberation of an active brominating agent, probably hypobromous acid, or a derivative of such, which is immediately reduced by the hydriodic acid:

$$:CHBr + H_2O = :CH_2 + HOBr.$$
$$HOBr + 2HI = HBr + H_2O + I_2$$

(compare Baeyer, *Annalen*, 1864, **130**, 133).

Evidence in favour of this explanation is afforded by the formation of tribromoaniline when dibromomalon-2:4-dibromoanilide is heated with hydrochloric acid in a sealed tube at 120°; such a reaction involves complete hydrolysis of the compound with formation of 2:4-dibromoaniline and an active brominating agent, which converts the dibromoaniline into tribromoaniline; this agent is most probably hypobromous acid formed by the hydrolysis of the $:CBr_2$ group:

$$CBr_2(CO{\cdot}NH{\cdot}C_6H_3Br_2)_2 + 4H_2O = CH_2(CO_2H)_2 + 2C_6H_3Br_2{\cdot}NH_2 + 2HOBr{\cdot}$$
$$C_6H_3Br_2{\cdot}NH_2 + HOBr = C_6H_2Br_3{\cdot}NH_2 + H_2O.$$

This evidence is strengthened by the fact that tribromoaniline is also formed when a mixture of dibromomalondiethylamide and 2:4-dibromoaniline is heated with hydrochloric acid in a sealed tube at 120°; in this case the source of the brominating agent is extra-molecular, and precludes the possibility of a wandering of bromine from the dibromomethylene complex to the dibromophenyl group, an explanation which might be suggested to account for the formation of tribromoaniline by the action of hydrochloric acid on dibromomalon-2:4-dibromoanilide.

It is hoped that the results of work now in progress will throw more light on this important aspect of the question. In the meantime, the present communication contains the account of the preparation of a series of *s*-di-alkyl- and -aryl-substituted derivatives of malonamide, and of the action of bromine on these compounds.

Action of Bromine on the Malondialkylamides.

With the exception of the *iso*propyl compound, the malondialkylamides are readily obtained by the condensation of ethyl malonate with the corresponding primary amine. In the case of the methyl and ethyl compounds, which are already known, the condensation takes place in aqueous solution at the ordinary temperature. The higher members of the series were obtained by heating the base with ethyl malonate in sealed tubes at 120—130°. Attempts to prepare malondi*iso*propylamide by this method were not successful; the condensation was not complete even after heating at 130° for six hours. The product was probably ethyl malon*iso*propylamate, but it was not identified owing to lack of sufficient material.

Malonamide and its dialkyl-substituted derivatives are readily *attacked by bromine, yielding the monobromomalonyl derivatives*, which on further treatment with bromine are converted into the corresponding dibromomalonyl compounds,

$$CH_2(CO{\cdot}NHR)_2 \longrightarrow CHBr(CO{\cdot}NHR)_2 \longrightarrow CBr_2(CO{\cdot}NHR)_2.$$

*With the exception of the dibromo-derivative of malondi-n-*butylamide (which has not been obtained in a crystalline form), these compounds are well-defined, colourless, crystalline substances, and each is quantitatively reduced to the corresponding malonyl derivative when a solution of the compound in cold glacial acetic *acid is mixed with a little solid potassium iodide and left for about* two hours.

Action of Bromine on the Aryl-substituted Derivatives of Malonamide.

The aryl-substituted malonamides that have been examined for their behaviour towards bromine are malonmonophenylamide, malonanilide, malon-*o*-toluidide, and malon-*p*-toluidide (Whiteley, T., 1903, **83**, 24; P., 1904, **20**, 92). These substances yield complex compounds owing to bromination of the malonyl and of the aromatic radicles.

Bromination of Malonanilide.—It might be expected that eight *of the twelve hydrogen atoms in malonanilide would be replaceable* by bromine by direct bromination, namely, the hydrogen atoms in the para- and the two ortho-positions in each phenyl group, and the two hydrogen atoms in the malonyl complex. The results obtained in this investigation show that only six of these hydrogen atoms are directly replaceable by bromine, these being the hydrogen atoms in the para- and one ortho-position in each phenyl group, and the hydrogen atoms in the malonyl group. Moreover, there is a marked difference in the readiness with which these hydrogen atoms are replaced, the reaction taking place in accordance with the following rules:

1. The hydrogen atom in the para-position in each phenyl group and one of the hydrogen atoms in the malonyl group are equally susceptible to the attack of bromine, and the first and least brominated derivative of malonanilide obtained is *bromomalon*-p-*bromoanilide.*

2. The second hydrogen atom in the malonyl radicle is more readily replaced than either of the hydrogen atoms in the ortho-positions in the phenyl groups; and the second product of bromination is *dibromomalon*-p-*bromoanilide.*

3. Only one of the two hydrogen atoms in the ortho-positions

in each phenyl group can be replaced by direct bromination, and the final product is therefore *dibromomalon-2 : 4-dibromoanilide.*

Although it has been found impossible to prepare, by direct bromination, a less brominated derivative of malonanilide than the tribromo-compound, or a more highly brominated derivative than the hexabromo-compound, derivatives of these types can be obtained by indirect methods. Dibromomalonanilide has been prepared by the condensation of dibromomalonyl chloride with aniline (Staudinger and Bereza, *Ber.*, 1908, **41**, 4465). *Dibromomalon*-2 : 4 : 6-*tribromoanilide* can be obtained by the direct bromination of malon-2 : 4 : 6-tribromoanilide. All attempts to prepare this derivative by the action of bromine on dibromomalon-2 : 4-dibromoanilide have been unsuccessful, this compound remaining unchanged after heating for twenty-four hours with a large excess of bromine in chloroform solution. Further, when bromomalon-*p*-bromoanilide in glacial acetic acid solution is heated at 100° for three days with excess of bromine and a trace of iodine, 2 : 4 : 6-tribromoaniline is formed; this somewhat unexpected reaction is explicable when considered in connexion with Freund's statement (*Ber.*, 1884, **17**, 782) that the hexabromo-derivative of malonanilide obtained by direct bromination yields tribromoaniline on hydrolysis with hydrochloric acid. On the strength of this evidence, Freund gave the name malon-2 : 4 : 6-tribromoanilide to his hexabromo-derivative, but the compound he obtained melted at 145° and was therefore dibromomalon-2 : 4-dibromoanilide, which melts at 146°, whilst malon-2 : 4 : 6-tribromoanilide has m. p. 331°. Moreover, we find that dibromomalon-2 : 4-dibromoanilide undergoes partial decomposition, yielding 2 : 4 : 6-tribromoaniline, when heated with concentrated hydrochloric acid in a sealed tube at 120° for twenty-four hours. The most probable explanation of this complex reaction is that dibromomalon-2 : 4-dibromoanilide is completely hydrolysed, yielding 2 : 4-dibromoaniline, malonic acid, and hypobromous acid, and the 2 : 4-dibromoaniline is converted into 2 : 4 : 6-tribromoaniline by the hypobromous acid:

$$CBr_2(CO{\cdot}NH{\cdot}C_6H_3Br_2)_2 + 4H_2O = 2C_6H_3Br_2{\cdot}NH_2 + 2HOBr + CH_2(CO_2H)_2.$$

$$C_6H_3Br_2{\cdot}NH_2 + HOBr = C_6H_2Br_3{\cdot}NH_2 + H_2O.$$

The formation of tribromoaniline during the prolonged action of bromine on bromomalon-*p*-bromoanilide can be similarly explained; the bromomalon-*p*-bromoanilide undergoes direct bromination, yielding dibromomalon-2 : 4-dibromoanilide, which is then hydrolysed as described above by the hydrobromic acid produced

in the reaction, and the dibromoaniline formed is converted into tribromoaniline by the excess of bromine present or by the hypobromous acid produced in the hydrolysis.

*Bromination of Malonmonophenylamide, Malon-*o*-toluidide, and Malon-*p*-toluidide.*

The bromination of malonmonophenylamide, malon-*o*-toluidide, and malon-*p*-toluidide accords with rules similar to those deduced in the case of malonanilide.

Malonmonophenylamide yields, on successive bromination, three products: *bromomalonmonobromophenylamide*, *dibromomalonmonobromophenylamide* and *dibromomalonmonodibromophenylamide*.

Malon-*o*-toluidide yields two products on successive bromination: *bromomalon-4-bromo-*o*-toluidide* and *dibromomalon-4-bromo-*o*-toluidide*.

Malon-*p*-toluidide yields three products on successive bromination: *bromomalon-*p*-toluidide*, *dibromomalon-*p*-toluidide*, and *dibromomalon-2-bromo-*p*-toluidide*.

The constitution of each of these compounds is readily determined, since the bromine in the malonyl complex is in all cases directly and quantitatively replaceable by hydrogen by the action of hydriodic acid.

EXPERIMENTAL.*

Malonamide.

Bromomalonamide, $CHBr(CO{\cdot}NH_2)_2$.—Attempts to prepare the monobromo-derivative of malonamide by the action of bromine (1 mol.) on an aqueous solution of malonamide (1 mol.) were unsuccessful. The bromine was rapidly absorbed, but the product was a mixture of the unchanged amide with the dibromo-derivative; when, however, the bromine was added to the amide dissolved in a sufficiently large excess of acetic acid to hold the amide in

* In all the analyses recorded in this paper, the *total* bromine was estimated by the method of Carius, Stepanoff, or Robinson. The *malonyl* bromine denotes the bromine that is replaced by hydrogen when the compound is reduced by hydrogen iodide under the following conditions: The compound (0·1—0·2 gram) is dissolved in cold, glacial acetic acid (about 50 c.c.), approximately 2 grams of powdered potassium iodide are added to the solution, the mixture is allowed to remain at the ordinary temperature for two hours, and the liberated iodine is titrated with a standard solution of sodium thiosulphate. A control experiment is made at the same time and a correction applied for the iodine liberated from potassium iodide by glacial acetic acid under the same conditions; this correction is very small if the acetic acid has been purified by preliminary treatment with potassium permanganate.

solution during the whole of the reaction, the product was the monobromo-derivative.

Five grams of malonamide (1 mol.) dissolved in 400 c.c. of glacial acetic acid were heated on the steam-bath, 25 c.c. of a 10 per cent. (by volume) solution of bromine in acetic acid (1 mol.) were added slowly, and the mixture was constantly shaken. The bromine was absorbed rapidly, and the reaction completed without the precipitation of any solid matter. After spontaneous evaporation of the solvent, slightly impure bromomalonamide (8·5 grams) was obtained in hard cubes which crystallised from ethyl alcohol in hard, colourless prisms melting and decomposing at 181°. [Found: Br (total) = 44·47; Br (malonyl) = 44·54. $CHBr(CO{\cdot}NH_2)_2$ requires Br = 44·17 per cent.].

Dibromomalonamide, $CBr_2(CO{\cdot}NH_2)_2$, is readily prepared by the action of bromine on a warm, aqueous solution of malonamide (Freund, *Ber.*, 1884, **17**, 782). The yield can be increased to 94 per cent. of that theoretically possible by the addition of sodium acetate equivalent to the hydrogen bromide liberated in the reaction. Dibromomalonamide is readily soluble in acetic acid, sparingly soluble in ethyl or methyl alcohol, acetone, or water, and insoluble in ethyl acetate, chloroform, carbon tetrachloride, or benzene. It crystallises in brilliant, colourless, octahedral prisms, m. p. 203° (without decomposition). Freund (*loc. cit.*) gives m. p. 206° with decomposition; Stokes and von Pechman (*Ber.*, 1886, **19**, 2699), and Staudinger (*Ber.*, 1908, **41**, 908) give m. p. 200° [Found: Br (malonyl) = 61·55. Calc., Br = 61·49 per cent.].

Malondimethylamide.

Bromomalondimethylamide, $CHBr(CO{\cdot}NHMe)_2$.—Eight grams (1 mol.) of malondimethylamide dissolved in 50 c.c. of chloroform were treated at 40—50° with 30 c.c. of a 10 per cent. (by volume) solution of bromine in the same solvent (1 mol.). The bromine was absorbed rapidly. After the solvent had evaporated, the semi-crystalline residue was dissolved in alcohol and the crystals which separated were filtered. The mother liquor, after being neutralised with anhydrous sodium carbonate, deposited a further quantity of crystals, from which acetone extracted the bromomalondimethylamide, the total amount being 9·4 grams. *Bromomalondimethylamide* is readily soluble in ethyl or methyl alcohol, ethyl acetate, acetone, acetic acid or chloroform, and is sparingly soluble in carbon tetrachloride, benzene, or light petroleum. It crystallises from ethyl-alcoholic solution in thin, colourless prisms, m. p. 164 [Found: N = 13·33; Br (total) = 38·50; Br (malonyl) = 38·20. $CHBr(CO{\cdot}NHMe)_2$ requires N = 13·4; Br = 38·24 per cent.].

Dibromomalondimethylamide, $CBr_2(CO{\cdot}NHMe)_2$, was prepared by Freund (*Ber.*, 1884, **17**, 782) by brominating malondimethylamide in warm, aqueous solution. He describes the compound as crystallising from concentrated, aqueous solution in thick, hard prisms, m. p. 162°. We find that the compound is more readily prepared by the action of excess of bromine on a hot solution of malondimethylamide or its monobromo-derivative in chloroform, and that it melts at 161°. Dibromomalondimethylamide dissolves very readily in water, ethyl or methyl alcohol or chloroform, less readily in ethyl acetate or acetone, sparingly in carbon tetrachloride, benzene, or light petroleum (b. p. 60—80°), and is insoluble in ether or light petroleum (b. p. 40—60°) [Found: Br (total) = 55·64; Br (malonyl) = 55·38. Calc., Br = 55·53 per cent.].

Malondiethylamide.

Malondiethylamide, $CH_2(CO{\cdot}NHEt)_2$, was prepared first by Wallach and Kamenski (*Ber.*, 1881, **14**, 170), who described it as crystallising in six-sided plates, m. p. 149°. Hausmann (*Annalen*, 1895, **285**, 97), obtained it as a by-product during the prolonged action of a benzene solution of ethylamine on ethyl 6-ethoxy-2-pyrone-3 : 5-dicarboxylate.

Malondiethylamide can be readily prepared in a yield of 95 per cent. of the theoretical by shaking a mixture of 16 grams of ethyl malonate (1 mol.), 30 grams of a 33 per cent. aqueous solution of ethylamine (2 mols.), and 0·2 gram of sodium hydroxide for about one hour at 0° until it is homogeneous. After remaining at the ordinary temperature for twelve hours, the solution is evaporated to dryness on the water-bath. Malondiethylamide dissolves very readily in ethyl or methyl alcohol, ethyl acetate, acetone, chloroform, or acetic acid, less readily in benzene, sparingly in carbon tetrachloride or light petroleum (b. p. 100—120°), and is insoluble in ether. After crystallising once from benzene, and once from a mixture of absolute alcohol and light petroleum (b. p. 40—60°), it melts at 149°.

Bromomalondiethylamide, $CHBr(CO{\cdot}NHEt)_2$, is obtained by brominating malondiethylamide in chloroform solution, the conditions being similar to those obtaining in the preparation of bromomalondimethylamide. From 8 grams of malondiethylamide 9·5 grams of crude product were obtained. *Bromomalondiethylamide* is very readily soluble in ethyl or methyl alcohol, ethyl acetate, acetone, or chloroform, sparingly soluble in benzene or in light petroleum (b. p. 100—120°), and insoluble in ether, carbon tetrachloride, or light petroleum (b. p. 60—80°). It crystallises from alcoholic or benzene solution in thin, colourless prisms, m. p. 160°

[Found: N = 11·81; Br (total) = 33·63; Br (malonyl) = 33·65. $C_7H_{13}O_2N_2Br$ requires N = 11·82; Br = 33·72 per cent.].

Dibromomalondiethylamide, $CBr_2(CO{\cdot}NHEt)_2$, is obtained from the monobromo-compound by further bromination. To 6·1 grams (1 mol.) of bromomalondiethylamide dissolved in chloroform were slowly added 20 c.c. of a 10 per cent. (by volume) solution of bromine in chloroform (1⅓ mols.) and the mixture was heated under reflux during four hours. After remaining at the ordinary temperature for a further twelve hours, the solvent and the excess of bromine were removed by spontaneous evaporation, the residual syrup was neutralised with solid sodium carbonate and allowed to evaporate to dryness, and the dibromomalondiethylamide extracted from the residue with dry ether; the yield was 98 per cent. of the theoretical. *Dibromomalondiethylamide* is very readily soluble in all the ordinary organic solvents with the exception of light petroleum (b. p. 40—60°), in which it is only sparingly soluble. When crystallised from a mixture of absolute alcohol and light petroleum (b. p. 40—60°) it separates in thin, colourless, prismatic needles that slowly change into large, hard prisms, m. p. 78° [Found: Br (total) = 50·71; Br (malonyl) = 50·38. $C_7H_{12}O_2N_2Br_2$ requires Br = 50·60 per cent.].

Malondi-n-*propylamide.*

Malondi-n-*propylamide*, $CH_2(CO{\cdot}NHPr^a)_2$.—A mixture of 7·05 grams of *n*-propylamine (2 mols.) and 9·6 grams of ethyl malonate (1 mol.) was allowed to remain in a sealed tube at the ordinary temperature for twenty-four hours, and was then heated at 125—130° for a further period of six hours. The product, after having been washed with petroleum, weighed 9·45 grams and was pure *malondi*-n-*propylamide*, m. p. 139°. It dissolves very readily in ethyl or methyl alcohol, ethyl acetate, acetic acid, chloroform, or carbon tetrachloride, less readily in acetone, benzene, or water, and sparingly in light petroleum (b. p. 60—80°); it crystallises from acetone in colourless, six-sided plates, m. p. 139° (Found: N = 15·18. $C_9H_{18}O_2N_2$ requires N = 15·07 per cent.).

Bromomalondi-n-*propylamide*, $CHBr(CO{\cdot}NHPr^a)_2$, is prepared similarly to bromomalondimethylamide by direct bromination of malondi-*n*-propylamide in chloroform solution, 2 grams of which yield 2·38 grams of the monobrominated amide. *Bromomalondi*-n-*propylamide* is very readily soluble in all the ordinary organic solvents with the exception of light petroleum (b. p. 60—80°, or 80—100°) and water, in which it is sparingly soluble. It is most conveniently crystallised from diluted alcohol, from which it separates in colourless, prismatic needles, m. p. 134·5° [Found:

$N = 10{\cdot}64$; Br (malonyl) $= 30{\cdot}15$. $C_9H_{17}O_2N_2Br$ requires $N = 10{\cdot}57$; $Br = 30{\cdot}16$ per cent.].

Dibromomalondi-n-*propylamide*, $CBr_2(CO{\cdot}NHPr^{\alpha})_2$, is conveniently obtained by further bromination of the monobromo-derivative in chloroform solution, as in the case of dibromomalondimethylamide, or by direct bromination of malondi-*n*-propylamide in hot, aqueous solution.

To 2·1 grams of malondi-*n*-propylamide (1 mol.) dissolved in 62 c.c. of boiling water, 4·78 grams of bromine (2⅝ mols.) were added in several, successive, small portions, the solution being well shaken after each addition. When about one-half of the bromine had been added, a colourless, crystalline product separated, which was probably the monobromo-compound, as it disappeared on the further addition of bromine. The final mixture consisted of an aqueous solution and a heavy, insoluble oil, each containing excess of bromine. This was removed by partial evaporation on the water-bath, and on cooling the mixture the oil solidified, and large, prismatic crystals separated from the aqueous solution. The total, dry solid weighed 3·5 grams and consisted of pure *dibromomalondi*-n-*propylamide*. This compound is very readily soluble in all the ordinary organic solvents with the exception of light petroleum (b. p. 40—60°), in which it is sparingly soluble. It is most conveniently crystallised from light petroleum (b. p. 60—80°), and forms colourless, hexagonal prisms, m. p. 78·5° [Found: $N = 8{\cdot}17$; Br (malonyl) $= 46{\cdot}14$. $C_9H_{16}O_2N_2Br_2$ requires $N = 8{\cdot}15$; $Br = 46{\cdot}49$ per cent.].

Malondi-n-*butylamide*.

Malondi-n-*butylamide*, $CH_2(CO{\cdot}NH{\cdot}C_4H_9)_2$, is readily obtained by the condensation of ethyl malonate with *n*-butylamine under similar conditions to those employed in the preparation of malondi-*n*-propylamide. 7·9 Grams of *n*-butylamine gave 9·61 grams of pure *malondi-n-butylamide*, m. p. 132·5°. The compound is readily soluble in ethyl or methyl alcohol, ethyl acetate, acetic acid, chloroform, acetone, carbon tetrachloride, or benzene, and sparingly soluble in water or light petroleum. It crystallises in pearly plates (Found: $N = 13{\cdot}01$. $C_{11}H_{22}O_2N_2$ requires $N = 13{\cdot}09$ per cent.).

Bromomalondi-n-*butylamide*, $CHBr(CO{\cdot}NH{\cdot}C_4H_9)_2$, prepared similarly to bromomalondimethylamide, is very readily soluble in all the ordinary organic solvents with the exception of light petroleum (b. p. 40—60°) and water, in which it is insoluble. It crystallises from a mixture of alcohol and water in thin, colourless prisms, m. p. 103° [Found: $N = 9{\cdot}62$; Br (malonyl) $= 26{\cdot}83$. $C_{11}H_{21}O_2N_2Br$ requires $N = 9{\cdot}57$; $Br = 27{\cdot}28$ per cent.].

*Malondi*isobutylamide.

*Malondi*isobutylamide, $CH_2(CO \cdot NH \cdot C_4H_9)_2$, was prepared similarly to malondi-*n*-butylamide by condensing ethyl malonate with *iso*butylamine. It dissolves very readily in ethyl or methyl alcohol, acetic acid, or chloroform, less readily in ethyl acetate, ether, acetone, or benzene, and is insoluble in light petroleum or in water; it crystallises from ethyl acetate in colourless needles, m. p. 126·5° (Found: N = 13·14. $C_{11}H_{22}O_2N_2$ requires N = 13·09 per cent.).

*Bromomalondi*isobutylamide, $CHBr(CO \cdot NH \cdot C_4H_9)_2$, is readily prepared by direct bromination of malondi*iso*butylamide. To a solution of 2 grams (1 mol.) of malondi*iso*butylamide in 10 c.c. of warm, glacial acetic acid were slowly added 4·7 c.c. of a 10 per cent. (by volume) solution of bromine in acetic acid (1 mol.); the bromine was rapidly absorbed. After remaining for ten minutes the solution was poured into 200 c.c. of water at 0°. The precipitated bromomalondi*iso*bntylamide from four such brominations weighed 8 grams, and crystallised from a mixture of benzene and light petroleum (b. p. 60—80°) in colourless, stout prisms, m. p. 151°. *Bromomalondi*isobutylamide is very readily soluble in cold ethyl or methyl alcohol, ethyl acetate, acetone, acetic acid, chloroform, or carbon tetrachloride, or in warm benzene, and sparingly soluble in light petroleum (b. p. 60—80°). It dissolves fairly readily in light petroleum (b. p. 80—100°) and the solution exhibits the property of forming a gel when rapidly cooled; after some time the gel slowly becomes limpid and deposits crystals [Found: N = 9·44; Br (total) = 27·4; Br (malonyl) = 27·21. $C_{11}H_{21}O_2N_2Br$ requires N = 9·57; Br = 27·28 per cent.].

*Gelatinisation of Solutions of Bromomalondi*isobutylamide *in Light Petroleum.**—Light petroleum, b. p. 73—76°, is the most convenient solvent; 100 c.c. dissolve 0·491 gram of bromomalondi*iso*butylamide at 50°. The solubility curve shows no transition point. Supersaturated solutions yield gels when cooled rapidly by immersing the vessel in cold water. A marked peculiarity is the capacity for gel formation in the presence of crystals; this condition obtains when saturated solutions at 70° are allowed to cool slowly without stirring. When a similar solution is stirred while cooling, there is no gel formation, and the dissolved solid is precipitated as a bulky mass of thin, needle-shaped crystals. The gel varies according to conditions, from complete transparency to opalescence; on heating it becomes opaque. When it is allowed to "set" on a microscope

* We are indebted to Miss Dorothy Haynes, B.Sc., D.I.C., for this report.

slide and afterwards gently warmed, a number of very small, stellate clusters of crystals can be observed under the microscope.

The gelatinisation appears to be due to the formation of highly dispersed, crystalline centres by sudden crystallisation in a medium in which diffusion takes place with difficulty; this explanation would also account for the co-existence of crystals and gel.

*Dibromomalondi*iso*butylamide*, $CBr_2(CO{\cdot}NH{\cdot}C_4H_9)_2$, is prepared by brominating malondi*iso*butylamide or its monobromo-derivative in carbon tetrachloride solution. To 2 grams of malondi*iso*butylamide (1 mol.) dissolved in 20 c.c. of warm carbon tetrachloride, 9·4 c.c. of a 10 per cent. (by volume) solution of bromine in carbon tetrachloride (2 mols.) were slowly added, the mixture was shaken, and warmed on the steam-bath from time to time until the reaction was completed. After the solvent had evaporated, the residual syrup yielded 3·18 grams of dibromomalondi*iso*butylamide when stirred with a mixture of alcohol and light petroleum (b. p. 40—60°). Two grams of bromomalondi*iso*butylamide on similar treatment yielded 2·48 grams of the dibromo-compound. *Dibromomalondi*iso*butylamide* dissolves readily in methyl or ethyl alcohol, benzene, or light petroleum (b. p. 60—80°), less readily in carbon tetrachloride or light petroleum (b. p. 40—60°), and crystallises in thin, colourless prisms, m. p. 100° [Found: Br (total) = 42·90; Br (malonyl) = 42·14. $C_{11}H_{20}O_2N_2Br_2$ requires Br = 42·98 per cent.].

Malondibenzylamide.

Malondibenzylamide, $CH_2(CO{\cdot}NH{\cdot}CH_2Ph)_2$, was readily prepared by gently boiling under reflux a mixture of 20 grams of ethyl malonate (1 mol.) and 27 grams of benzylamine (2 mols.) for about twenty hours. The product solidified on cooling, and after having been washed with alcohol weighed 30 grams. *Malondibenzylamide* is readily soluble in ethyl or methyl alcohol, acetic acid, or chloroform, sparingly soluble in ethyl acetate, acetone, benzene, or water, and insoluble in ether; it crystallises in colourless plates, m. p. 142° (Found: N = 10·03. $C_{17}H_{18}O_2N_2$ requires N = 9·93 per cent.).

Bromomalondibenzylamide, $CHBr(CO{\cdot}NH{\cdot}CH_2Ph)_2$, is the first product of the bromination of malondibenzylamide. To 2 grams of malondibenzylamide (1 mol.) dissolved in 12 c.c. of hot, glacial acetic acid, 3·6 c.c. of a 10 per cent. (by volume) solution of bromine in acetic acid (1 mol.) were slowly added. The bromine was rapidly absorbed and the addition of hot water to the acetic acid solution caused the precipitation of the bromomalondibenzylamide in a crystalline form; the yield was quantitative. *Bromomalondibenzylamide* is readily soluble in ethyl or methyl alcohol, ethyl acetate, acetone, or chloroform, and sparingly soluble in carbon tetrachloride,

benzene, or light petroleum (b. p. 100—120°). It crystallises in thin, colourless needles, m. p. 167° [Found: N = 7·79; Br (total) = 22·21; Br (malonyl) = 22·02. $C_{17}H_{17}O_2N_2Br$ requires N = 7·76; Br = 22·16 per cent.].

Dibromomalondibenzylamide, $CBr_2(CO{\cdot}NH{\cdot}CH_2Ph)_2$.—Considerable difficulty was experienced at first in preparing the dibromo-derivative of malondibenzylamide. Exhaustive bromination of the amide itself or of its monobromo-derivative gave mixed crystals of the mono- and di-bromo-derivatives, containing about eight parts of the former and ninety-two parts of the latter, and similar mixtures were afforded by the condensation of dibromomalonyl chloride with benzylamine, owing, probably, to the presence of a small quantity of monobromomalonyl chloride as an impurity in the dibromo-compound; these crystals melted at 139°.

A solution of 2 grams of malondibenzylamide in carbon tetrachloride was mixed with an amount of bromine dissolved in the same solvent in excess of that required for the formation of the dibromo-compound, and the mixture boiled under reflux until the excess of bromine was expelled. The mixture of crystals and syrup remaining after the spontaneous evaporation of the solvent was washed with alcohol and yielded 3·65 grams of a mixture of the mono- and di-bromo-derivatives in colourless crystals. It was dissolved in a hot solution of bromine in carbon tetrachloride and the solution boiled until heavy, prismatic crystals of the dibromo-compound separated from the boiling solution, which still contained free bromine. The crystals, after having been washed with alcohol, weighed 2·95 grams. *Dibromomalondibenzylamide* dissolves readily in ethyl or methyl alcohol, ethyl acetate, acetone, acetic acid, chloroform, or benzene, less readily in carbon tetrachloride or light petroleum (b. p. 100—120°), and sparingly in ether or light petroleum (b. p. 60—80°); it forms hard, prismatic, colourless crystals, m. p. 128°. The melting point is raised by the admixture of a very small quantity of the monobromo-derivative [Found: N = 6·36; Br (total) = 36·09; Br (malonyl) = 36·43. $C_{17}H_{16}O_2N_2Br_2$ requires N = 6·36; Br = 36·34 per cent.].

Malonyldiurethane.

Malonyldiurethane, $CH_2(CO{\cdot}NH{\cdot}CO_2Et)_2$, m. p. 124°, was prepared by Conrad and Schulze (*Ber.*, 1909, **42**, 734) by condensing malonic acid with urethane in acetic anhydride solution. It is more conveniently obtained by warming a mixture of 10 grams of malonic acid (1 mol.), 18 grams of urethane (2 mols.), and 16 c.c. of phosphoryl chloride (2 mols.), with constant stirring at about 80° until hydrogen chloride is no longer evolved copiously. The

resinous product yields crystalline malonyldiurethane, m. p. 124°, on treatment with cold water; the yield, 71 per cent. of the theoretical, is the same as that obtained by Conrad and Schulze (*loc. cit.*).

Bromomalonyldiurethane, $CHBr(CO\cdot NH\cdot CO_2Et)_2$, is readily prepared by heating for a few minutes a mixture of 2 grams of malonyldiurethane and an excess of bromine in chloroform solution. After the solvent and the excess of bromine have been allowed to evaporate the semi-solid residue is washed with ether, when 2·65 grams of the crude monobromo-compound are obtained. *Bromomalonyldiurethane* is very readily soluble in ethyl or methyl alcohol, ethyl acetate, acetone, or acetic acid, sparingly soluble in water, and insoluble in chloroform, carbon tetrachloride, or benzene; it crystallises from a mixture of alcohol and water in colourless prisms that melt with slight decomposition at 148° [Found: N = 8·72; Br (total) = 24·47; Br (malonyl) = 24·79. $C_9H_{13}O_6N_2Br$ requires N = 8·64; Br = 24·61 per cent.].

All attempts to prepare a *dibromo*-derivative of malonyldiurethane were unsuccessful; bromomalonyldiurethane is not changed by treatment with bromine in chloroform or acetic acid solution even at the boiling point of the solution.

Malonmonophenylamide.

A mixture of 15 grams of aniline (1 mol.) and 36 grams of ethyl malonate (1·5 mols.) was heated at 120° under reflux for six hours. The liquid, when cold, was shaken with twice its volume of concentrated ammonia solution for two hours and the excess of ammonia and one-half of the water then evaporated on the steam-bath. On cooling, *malonmonophenylamide* (24 grams) crystallised from the solution; malonamide (6 grams) was recovered from the mother liquor.

Malonmonophenylamide, $NH_2\cdot CO\cdot CH_2\cdot CO\cdot NHPh,\frac{1}{2}H_2O$, crystallises from a hot aqueous solution in colourless, pearly plates containing water of crystallisation, which it loses at 100°. The hydrated crystals melt indefinitely at 130—134°, the anhydrous substance at 164°. *Malonmonophenylamide* is readily soluble in all the ordinary organic solvents with the exception of chloroform, carbon tetrachloride, and light petroleum [Found: H_2O = 4·98; N = 15·77. $C_9H_{10}O_2N_2,\frac{1}{2}H_2O$ requires H_2O = 4·81; N = 15·73 per cent.].

Bromomalonmonobromophenylamide,

$NH_2\cdot CO\cdot CHBr\cdot CO\cdot NH\cdot C_6H_4Br$*.

A solution of 4·5 grams (1 mol.) of malonmonophenylamide in

* The position of the bromine atom in the phenyl group in this compound has not been determined. It is most probably in the para-position.

50 c.c. of glacial acetic acid was treated with 25 c.c. of a 10 per cent. (by volume) solution of bromine in the same solvent (2 mols.). After heating at 100° for thirty minutes, the bromine was almost entirely absorbed. The solution was allowed to evaporate to dryness and the residual *bromomalonmonobromophenylamide* crystallised from ethyl alcohol, when it was obtained in colourless needles melting and decomposing at 200°; the yield was 91 per cent. of the theoretical [Found: Br (total) = 47·61; Br (malonyl) = 23·98. $C_9H_8O_2N_2Br_2$ requires Br (total) = 47·60; Br (malonyl) = 23·81 per cent.].

Dibromomalonmonobromophenylamide,

$NH_2·CO·CBr_2·CO·NH·C_6H_4Br$,*

was prepared by heating malonmonophenylamide (4·5 grams; 1 mol.) and bromine (3·5 mols.) in acetic acid solution at 100° for one hour. On shaking vigorously, large quantities of hydrogen bromide were evolved and *dibromomalonmonobromophenylamide* separated as a crystalline solid. After crystallising from alcohol, it formed stout, colourless prisms, m. p. 142°, the yield being 85 per cent. of the theoretical [Found: N = 6·51; Br (total) = 57·90; Br (malonyl) = 38·22. $C_9H_7O_2N_2Br_3$ requires N = 6·75; Br (total) = 57·81; Br (malonyl) = 38·54 per cent.].

Dibromomalonmonodibromophenylamide,

$NH_2·CO·CBr_2·CO·NH·C_6H_3Br_2$,†

was obtained by treating 5 grams (1 mol.) of dibromomalonmonobromophenylamide dissolved in 100 c.c. of hot glacial acetic acid with a large excess of bromine (10 c.c.) and allowing the solution to remain at the ordinary temperature during five days. It separated in well-formed, colourless prisms, which, after crystallisation from alcohol, melted at 174° [Found: Br (total) = 64·76; Br (malonyl) = 31·95. $C_9H_6O_2N_2Br_4$ requires Br (total) = 64·76; Br (malonyl) = 32·38 per cent.].

The product obtained by reducing dibromomalonmonodibromophenylamide by hydriodic acid is *malonmonodibromophenylamide*, $NH_2·CO·CH_2·CO·NH·C_6H_3Br_2$; it crystallises from dilute alcohol in stout, colourless prisms, m. p. 194° (decomp.) [Found: Br = 47·89. $C_9H_8O_2N_2Br_2$ requires Br = 47·60 per cent.].

Malonanilide.

Bromomalon-p-bromoanilide, $CHBr(CO·NH·C_6H_4Br)_2$.—To 20 grams (1 mol.) of malonanilide dissolved in 250 c.c. of hot glacial

* The position of the bromine atom in the phenyl group in this compound has not been determined. It is most probably in the para-position.

† The positions of the bromine atoms in the phenyl radicles of this compound have not been determined; they are most probably in the 2:4 positions.

acetic acid 135 c.c. of a 10 per cent. (by volume) solution of bromine in chloroform (3·5 mols.) were added drop by drop. The bromine was absorbed rapidly, and on vigorous shaking hydrogen bromide was expelled copiously and *bromomalon*-p-*bromoanilide* was deposited as a heavy, white, crystalline solid. This was filtered while hot, and after crystallising from a mixture of benzene and absolute alcohol obtained in thin, colourless, silky needles, m. p. 236° [Found: Br (total) = 49·06; Br (malonyl) = 16·01. $C_{15}H_{11}O_2N_2Br_3$ requires Br (total) = 48·88; Br (malonyl) = 16·29 per cent.].

Proofs that the constitution of the compound is as designated were afforded (1) by the preparation of the same compound by direct bromination of malon-*p*-bromoanilide, m. p. 268°, obtained by condensing *p*-bromoaniline with ethyl malonate (Chattaway and Mason, T., 1910, **97**, 340); and (2) by the formation of malon-*p*-bromoanilide, m. p. 268°, on reducing the compound with hydriodic acid,

$$CH_2(CO{\cdot}NH{\cdot}C_6H_4Br)_2 \underset{2HI}{\overset{Br_2}{\rightleftarrows}} CHBr(CO{\cdot}NH{\cdot}C_6H_4Br)_2.$$

Dibromomalon-p-*bromoanilide*, $CBr_2(CO{\cdot}NH{\cdot}C_6H_4Br)_2$.—To 15 grams (1 mol.) of bromomalon-*p*-bromoanilide dissolved in 1 litre of boiling glacial acetic acid, 30 c.c. of a 10 per cent. (by volume) solution of bromine in chloroform (2 mols.) were added drop by drop. The bromine was not absorbed rapidly, but after remaining for fifty to sixty hours at the ordinary temperature the bromine disappeared and *dibromomalon*-p-*bromoanilide* was obtained as a heavy, glassy, crystalline substance. It had m. p. 164° and formed well-defined, colourless prisms [Found: Br (total) = 56·02; Br (malonyl) = 28·09. $C_{15}H_{10}O_2N_2Br_4$ requires Br (total) = 56·11; Br (malonyl) = 28·05 per cent.].

Malon-*p*-bromoanilide, m. p. 268°, was obtained by reducing the compound with hydriodic acid.

Dibromomalon-2:4-*dibromoanilide*, $CBr_2(CO{\cdot}NH{\cdot}C_6H_3Br_2)_2$, was prepared by treating a hot solution of 15 grams (1 mol.) of bromomalon-*p*-bromoanilide in 450 c.c. of glacial acetic acid with 36 c.c. (23·5 mols.) of bromine. After standing about six hours at the ordinary temperature the precipitate of very thin, needle-shaped crystals which had separated was collected, washed, and recrystallised from a mixture of benzene and alcohol, when *dibromomalon*-2:4-*dibromoanilide* was obtained in colourless needles, m. p. 146° [Found: Br (total) = 66·19; Br (malonyl) = 22·20. $C_{15}H_8O_2N_2Br_6$ requires Br (total) = 65·92; Br (malonyl) = 21·97 per cent.].

The compound obtained by reducing dibromomalon-2:4-dibromoanilide with hydriodic acid melts at 231° and is identical

with the malon-2 : 4-dibromoanilide prepared by condensing ethyl malonate with 2 : 4-dibromoaniline. Chattaway and Mason (*loc. cit.*), who first prepared malon-2 : 4-dibromoanilide, found that it had m. p. 233°.

Dibromomalon-2 : 4-dibromoanilide yields 2 : 4 : 6-tribromoaniline when hydrolysed with hydrochloric acid under the following conditions : 2 grams of the anilide and 15 c.c. of concentrated hydrochloric acid were heated at 120° in a sealed tube for twenty-four hours. When cold, the tube contained colourless, needle-shaped crystals together with unchanged dibromomalon-2 : 4-dibromoanilide. The solid was filtered, extracted with hot hydrochloric acid, and the filtrate and extract neutralised with alkali, when 2 : 4 : 6-tribromoaniline, m. p. 120°, was obtained.

Dibromomalon-2 : 4 : 6-tribromoanilide, $CBr_2(CO{\cdot}NH{\cdot}C_6H_2Br_3)_2$.—Five grams (1 mol.) of malon-2 : 4 : 6-tribromoanilide (Chattaway and Mason, *loc. cit.*) were ground into a thin paste with 150 c.c. of dry chloroform, mixed with a large excess (15 c.c.) of bromine, and heated to gentle ebullition on the water-bath. After forty-five minutes all the solid had dissolved and the chloroform and excess of bromine were allowed to evaporate spontaneously. The residual, dry solid, after crystallising from carbon tetrachloride, formed flat, colourless prisms, m. p. 174°, and was *dibromomalon-2 : 4 : 6-tribromoanilide* [Found : Br (total) = 72·46 ; Br (malonyl) = 17·75. $C_{15}H_6O_2N_2Br_8$ requires Br (total) = 72·22 ; Br (malonyl) = 18·05 per cent.].

Dibromomalonanilide, $CBr_2(CO{\cdot}NHPh)_2$, was prepared by Staudinger and Bereza (*Ber.*, 1908, **41**, 4465) by condensing dibromomalonyl chloride with aniline and crystallising the product from methyl alcohol; the crystals thus obtained melted at 143—144° and contained N = 7·16 per cent. ($C_{15}H_{12}O_2N_2Br_2$ requires N = 6·80 per cent.). We used the same method to prepare the dibromomalonanilide required in this investigation, and obtained a similar product, which crystallised from methyl alcohol in large, well-defined, highly refractive prisms and melted at 144°. The material was not pure, however, and by repeated crystallisation from methyl alcohol or light petroleum (b. p. 100—120°) it was separated into *dibromomalonanilide* [Found : N = 6·92 ; Br (total) = 38·91 ; Br (malonyl) = 34·09. $C_{15}H_{12}O_2N_2Br_2$ requires Br (total and malonyl) = 38·82 ; N = 6·80 per cent.], which formed hard, compact, heavy prisms, m. p. 147°, and a very small quantity of a *compound*, m. p. 171°, that crystallised in thin, silky needles, and has not been identified owing to lack of material.

The chief product of the reducing action of hydriodic acid on dibromomalonanilide is malonanilide, m. p. 225°, but another crystalline compound is also formed in small amount and this has

not yet been isolated in sufficient quantity for identification. It is not improbable that the low value obtained for the malonyl bromine in dibromomalonanilide may be connected with the formation of this by-product.

Malon-p-*toluidide.*

Bromomalon-p-*toluidide*, $CHBr(CO{\cdot}NH{\cdot}C_7H_7)_2$, was prepared by the action of a solution of bromine (1 mol.) in chloroform on a hot acetic acid solution of 7 grams (1 mol.) of malon-*p*-toluidide. The bromine was absorbed very rapidly; the *bromomalon*-p-*toluidide*, which separated as a heavy, granular precipitate, was crystallised from a mixture of benzene and alcohol and obtained in thin, colourless plates melting at 211°. [Found: Br (total) = 21·94; Br (malonyl) = 22·30. $C_{17}H_{17}O_2N_2Br$ requires Br = 22·14 per cent.].

Malon-*p*-toluidide, m. p. 251°, was obtained by reducing the bromo-compound with hydriodic acid.

Dibromomalon-p-*toluidide*, $CBr_2(CO{\cdot}NH{\cdot}C_7H_7)_2$, was prepared by heating gently a mixture of 6 grams (1 mol.) of bromomalon-*p*-toluidide and bromine (1 mol.) in chloroform for about three hours. The solution was cooled, filtered from a little unchanged monobromo-compound, and the filtrate allowed to evaporate spontaneously to dryness. The residual, crude dibromomalon-*p*-toluidide was washed with ether and recrystallised from carbon tetrachloride, when it formed short, colourless, prismatic needles melting at 137° [Found: Br (total) = 36·06; Br (malonyl) = 35·96. $C_{17}H_{16}O_2N_2Br_2$ requires Br = 36·34 per cent.].

Malon-*p*-toluidide, m. p. 251°, was obtained by the action of hydriodic acid on the dibromo-compound.

Dibromomalon-2-bromo-p-*toluidide*, $CBr_2(CO{\cdot}NH{\cdot}C_7H_6Br)_2$, was prepared by heating under reflux 5 grams (1 mol.) of finely divided malon-*p*-toluidide and bromine (8 mols.) in chloroform until all the solid had dissolved. The cold solution was allowed to evaporate spontaneously, and the residual *dibromomalon-2-bromo*-p-*toluidide* crystallised from alcohol or carbon tetrachloride, when it was obtained as short, colourless prisms, m. p. 150° [Found: Br (total) = 53·64; Br (malonyl) = 26·99. $C_{17}H_{14}O_2N_2Br_4$ requires Br (total) = 53·50; Br (malonyl) = 26·75 per cent.].

The compound obtained by reducing dibromomalon-2-bromo-*p*-toluidide by hydriodic acid melts at 180°, and is identical with *malon-2-bromo*-p-*toluidide* prepared by condensing ethyl malonate with 2-bromo-*p*-toluidine (Found: Br = 35·98. $C_{17}H_{16}O_2N_2Br_2$ requires Br = 36·34 per cent.).

Malon-o-toluidide.

Bromomalon-4-bromo-o-toluidide, $CHBr(CO{\cdot}NH{\cdot}C_7H_6Br)_2$, was prepared by slowly treating a hot acetic acid solution of 10 grams (1 mol.) of malon-*o*-toluidide with a solution of bromine (3·4 mols.) in chloroform. After all the bromine had been added the heating was continued for a further thirty minutes, when *bromomalon-4-bromo-o-toluidide* separated as a white, crystalline precipitate. After recrystallisation from acetic acid, it formed colourless needles, m. p. 233° [Found: Br (total) = 46·31; Br (malonyl) = 15·16. $C_{17}H_{15}O_2N_2Br_3$ requires Br (total) = 46·22; Br (malonyl) = 15·41 per cent.].

The reduced product obtained by the action of hydriodic acid on this tribromo-derivative melts at 216°, and is identical with the *malon-4-bromo-o-toluidide* prepared by condensing ethyl malonate with 4-bromo-*o*-toluidine.

Dibromomalon-4-bromo-o-toluidide, $CBr_2(CO{\cdot}NH{\cdot}C_7H_6Br)_2$.—To a solution of 3 grams of bromomalon-4-bromo-*o*-toluidide in 750 c.c. of acetic acid a solution of bromine (1·5 mols.) in chloroform was added. After remaining for twenty-four hours at the ordinary temperature, the bromine had almost entirely disappeared, and on partial evaporation of the solvent *dibromomalon-4-bromo-o-toluidide* separated in well-defined, thin prisms, and after crystallising from carbon tetrachloride melted at 138° [Found: Br (total) = 53·78; Br (malonyl) = 27·09. $C_{17}H_{14}O_2N_2Br_4$ requires Br (total) = 53·49; Br (malonyl) = 26·74 per cent.].

Malon-4-bromo-o-toluidide is obtained by reducing dibromomalon-4-bromo-*o*-toluidide with hydriodic acid. It is readily soluble in acetic acid, and on dilution with water is precipitated as a bulky, curdy mass, which can be filtered and dried only with difficulty. It crystallises from a mixture of acetic acid and alcohol, or from alcohol, in colourless, prismatic crystals, m. p. 216° (slight decomp.) (Found: N = 6·41. $C_{17}H_{16}O_2N_2Br_2$ requires N = 6·37 per cent.).

Reduction of Ureides of Mono- and Di-bromomalonic Acids by Hydriodic Acid.

Dibromobarbituric Acid.—The dibromobarbituric acid used in this analysis was colourless and crystalline, and melted and decomposed at 234° [Found: Br (malonyl) = 54·95. Calc.: Br (malonyl) = 55·92 per cent.].

It was observed by Baeyer (*Annalen*, 1864, **130**, 133) that there is a difference in the reactivity of the two bromine atoms in dibromobarbituric acid, one of these being more readily replaced

by hydrogen than the other. We find that the reduction of dibromobarbituric acid is effected to the extent of one-half of the bromine present when a neutral solution of potassium iodide is added to an aqueous solution of the acid [Found : Br (malonyl) = 27·38 per cent.].

5-*Bromo*-1 : 3-*diphenylbarbituric acid*, $CO{<}^{NPh\cdot CO}_{NPh\cdot CO}{>}CHBr$, was prepared by adding slowly 13 c.c. of a 10 per cent. solution of bromine in chloroform (1 mol.) to a warm solution of 7 grams of 1 : 3-diphenylbarbituric acid (1 mol.) in 50 c.c. of chloroform. The bromine was absorbed rapidly, and on spontaneous evaporation of the solvent and washing the residual solid with light petroleum (b. p. 40—60°) a quantitative yield of 5-*bromo*-1 : 3-*diphenylbarbituric acid* was obtained. It crystallised from carbon tetrachloride or light petroleum (b. p. 100—120°) in hard, crystalline warts, m. p. 155°, and was very readily soluble in all the ordinary organic solvents [Found : Br (total) = 22·35; Br (malonyl) = 22·38. $C_{16}H_{11}O_3N_2Br$ requires Br = 22·20 per cent.].

5 : 5-Dibromo-1 : 3-diphenylbarbituric acid,

$$CO{<}^{NPh\cdot CO}_{NPh\cdot CO}{>}CBr_2,C_6H_6,$$

(Whiteley, T., 1907, **91**, 1330), is quantitatively reduced by hydriodic acid to 1 : 3-diphenylbarbituric acid [Found : Br (malonyl) = 31·06. Calc. : Br (malonyl) = 30·99 per cent.].

5-Bromo-5-benzoyl-1 : 3-diphenylbarbituric acid, m. p. 186° (Whiteley, P., 1908, **24**, 278), is quantitatively reduced by hydriodic acid to 5-benzoyl-1 : 3-diphenylbarbituric acid [Found : Br (malonyl) = 17·60. Calc. : Br (malonyl) = 17·27 per cent.].

5-Bromo-2-thio-1 : 3-diphenylbarbituric acid, m. p. 220° (Whiteley, *loc. cit.*), is reduced quantitatively to 2-thio-1 : 3-diphenylbarbituric acid by the action of hydriodic acid [Found : Br (malonyl) = 20·40; N = 7·56; S = 8·79. Calc. : Br (malonyl) = 21·31; N = 7·47; S = 8·55 per cent.].

5 : 5-Dibromo-2-thio-1 : 3-diphenylbarbituric acid, m. p. 190° (Whiteley, *loc. cit.*), is reduced quantitatively to 2-thio-1 : 3-diphenylbarbituric acid by the action of hydriodic acid [Found : Br (malonyl) = 34·66; N = 6·21; S = 7·23. Calc. : Br (malonyl) = 35·22; N = 6·17; S = 7·07 per cent.].

Reduction of some Typical Bromo-ketones by Hydriodic Acid.

ω-Bromoacetophenone.—0·1281 Gram dissolved in 10 c.c. of acetic acid and mixed with 10 c.c. of a 10 per cent. solution of potassium iodide liberated iodine equivalent to 25·86 c.c. of *N*/20-iodine solution (Br = 40·34. Calc. : Br = 40·17 per cent.).

Phenyl αβ-dibromo-β-phenylethyl Ketone.—0·0843 Gram dissolved in acetic acid containing potassium iodide liberated iodine equivalent to 9·09 c.c. of $N/20$-iodine solution [Br (replaceable) = 21·55. Calc.: Br (replaceable) = 21·72 per cent.].

α-Bromo-α-nitrocamphor.—0·2108 Gram dissolved in acetic acid and mixed with 10 c.c. of a 10 per cent. solution of potassium iodide liberated instantaneously iodine equivalent to 30·74 c.c. of $N/20$-iodine solution (Br = 29·13. Calc.: Br = 28·97 per cent.).

The reduction of α-bromo-α-nitrocamphor with the liberation of two equivalents of iodine is also effected instantaneously when a neutral solution of potassium iodide is added to an alcoholic solution of the compound. In this respect bromonitrocamphor behaves like ethyl bromonitromalonate (Willstätter and Hottenroth, *Ber.*, 1904, **37**, 1775).

I am happy to have this opportunity of expressing my thanks to the Federation of University Women for the award of a Fellowship which facilitated the prosecution of this research.—M. A. W.

My best thanks are due to the Advisory Council of the Scientific and Industrial Research Department for a grant which has defrayed part of the cost of this investigation.—J. V. B.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, S.W. [*Received, December 18th, 1920.*]

XLV.—*The Formation and Properties of Dithioketones* ($R_2C{:}S{:}S$) *and Dithio-ethers* ($R_2S{:}S$). *Part I.*

By KUVERJI GOSAI NAIK.

THE formation of "mustard gas" (ββ′-dichlorodiethyl sulphide) by the sulphur chloride process may be represented by the scheme:

$$2CH_2{:}CH_2 + Cl_2S{:}S \begin{cases} \rightarrow (CH_2Cl{\cdot}CH_2)_2S{:}S \quad \text{(I.)} \\ \rightarrow (CH_2Cl{\cdot}CH_2)_2S + S. \quad \text{(II.)} \end{cases}$$

Certain difficulties were initially encountered owing to the condition in which the second sulphur atom occurred in the product. If the reaction between sulphur monochloride and ethylene is carried out under the right conditions the second atom of sulphur is deposited in the elemental form, but under other conditions it remains either in solution in or in combination with the sulphide

(II). The question whether the compound (I) is stable under ordinary atmospheric conditions is a vital one, because the vapour tension of "mustard gas" is already so low as to place it on the line limiting the usefulness in war of toxic substances which rely for their effect on the amount of vapour introduced into the air under normal conditions of temperature and pressure. If the second sulphur atom remained in chemical combination, as in formula I, the vapour tension of the compound would be lower than that of "mustard gas," and its utility as a toxic agent would thereby be diminished, if not entirely destroyed.

The late Lieut.-Col. Harrison showed that the product containing the two sulphur atoms vaporised completely at the ordinary temperature, leaving only a residue of sulphur, and that the vapour evolved at different periods of the evaporation had the same order of toxicity as "mustard gas."

There is thus no doubt that the second sulphur atom in the product of the action of sulphur monochloride on ethylene behaves as if it were in solution in, and not in chemical combination with, the sulphide, and the objects of the present series of investigations are to show to what degree the instability of the dithio-grouping is affected by the molecular condition of the remainder of the molecule and to compare the relative stability exhibited by corresponding dithio-ketones of the general formula $R_2C{:}S{:}S$.

The first compound of the dithio-ketone series (III) was prepared by the action of sulphur monochloride on malonanilide in accordance with the equation :

$$(NHPh{\cdot}CO)_2CH_2 + Cl_2S{:}S = \underset{\text{(III.)}}{(NHPh{\cdot}CO)_2C{:}S{:}S} + 2HCl.$$

The formula given to it above is proved by the following considerations :

(1) It is a dithio-ketone, that is, it is formed from one molecule of the anilide and one molecule of sulphur monochloride with the elimination of two hydrogen atoms as hydrogen chloride.

(2) The two hydrogen atoms are not supplied by the phenyl groups, because a dithio-ketone (IV) is produced from malondimethylamide by a similar reaction :

$$(NHMe{\cdot}CO)_2CH_2 + Cl_2S{:}S = \underset{\text{(IV.)}}{(NHMe{\cdot}CO)_2C{:}S{:}S} + 2HCl$$

also

$$(CH_2Ph{\cdot}NH{\cdot}CO)_2CH_2 + Cl_2S{:}S = \underset{\text{(V.)}}{(CH_2Ph{\cdot}NH{\cdot}CO)_2C{:}S{:}S} + 2HCl.$$

(3) The two hydrogen atoms eliminated are not those which were originally attached to the two nitrogen atoms, because when

sulphur monochloride reacts with methylmalonanilide (VI)—which, it will be noted, cannot form a dithio-ketone on the methine carbon atom, but can readily do so if the two hydrogen atoms attached to nitrogen are those affected—there is formed a disulphide (VII) in accordance with the equation :

$$2CHMe(CO{\cdot}NHPh)_2 \xrightarrow{Cl_2S:S} S:S<\begin{matrix}CMe(CO{\cdot}NHPh)_2\\ CMe(CO{\cdot}NHPh)_2\end{matrix}.$$

(VI.) (VII.)

Similar disulphides are produced when tertiary alkylated amides are employed. Thus the disulphide (VIII) is produced from malondimethylanilide :

$$2CH_2(CO{\cdot}NMePh)_2 \longrightarrow S:S<\begin{matrix}CH(CO{\cdot}NMePh)_2\\ CH(CO{\cdot}NMePh)_2\end{matrix}.$$

(VIII.)

It should be added that these disulphides, unlike the dithio-derivative of " mustard gas " to which they are apparently related in composition, are stable substances. They are at present under investigation.

(4) The dithio-ketones behave on hydrolysis in a manner which is in accordance with that which might be expected from the proposed formula. Thus, dithiomesoxanilide (III), on hydrolysis with alkali hydroxides, yields aniline and the alkali salt of a dithio-acid which probably has the structure IX, because it yields hydrogen sulphide by treatment with mineral acids :

$$\underset{(III.)}{S:S:C(CO{\cdot}NHPh)_2} \xrightarrow{KOH} PhNH_2 + \underset{(IX.)}{S:S:C(CO_2K)_2}.$$

(5) When dithiomesoxanilide (III) is treated with bromine, sulphur bromide is produced, together with the compound (X), which is identical with that formed by the action of bromine on malonanilide (Backes, West, and Whiteley, this vol., p. 373). It is evident therefore that the reaction takes place thus :

$$S:S:C(CO{\cdot}NHPh)_2 + 3Br_2 \rightarrow SBr{\cdot}SBr:C(CO{\cdot}NH{\cdot}C_6H_4Br)_2 + 2HBr$$
$$\rightarrow S_2Br_2 + \underset{(X.)}{CHBr(CO{\cdot}NH{\cdot}C_6H_4Br)_2}.$$

(6) On reduction with an alkaline solution of sodium hydrosulphide dithiomesoxanilide is transformed into malonanilide and hydrogen sulphide :

$$S:S:C(CO{\cdot}NHPh)_2 + 6H = 2H_2S + CH_2(CO{\cdot}NHPh)_2.$$

(7) The action of sulphur monochloride on diphenylbarbituric acid also yields a dithio-ketone (XI) :

$$CH_2<\begin{matrix}CO{\cdot}NPh\\ CO{\cdot}NPh\end{matrix}>CO \xrightarrow{Cl_2S:S} S:S:C<\begin{matrix}CO{\cdot}NPh\\ CO{\cdot}NPh\end{matrix}>CO.$$

(XI.)

It is clear, therefore, that the formulæ assigned to the dithio-ketones are correct. It may be added that their stability is such that the action of fuming nitric acid on, for example, dithiomesoxanilide leads to the formation of a tetranitro-compound (XII) and leaves the dithio-group intact :

$$S{:}S{:}C(CO{\cdot}NHPh)_2 \longrightarrow \underset{\text{(XII.)}}{S{:}S{:}C(CO{\cdot}NH{\cdot}C_6H_3[NO_2]_2)_2}$$

Already, therefore, compounds of both dithio-ketone and dithio-ether types have been isolated which exhibit a degree of stability altogether different from that of the hypothetical dithio-derivative formed in the "mustard gas" reaction. It is perhaps too soon to draw any definite conclusion, but the difference is so great that one is forced to consider whether in these reactions sulphur monochloride may not react in two forms, namely, SCl·SCl and $Cl_2S{:}S$. This question has led to much controversy, and the general opinion at the present time is that the second formula is the correct one. Indeed, it would be difficult to explain the formation of "mustard gas" on any other assumption. Still, if it can be assumed that the reagent can react in either form according to the conditions of the experiment and that in the experiments described in the present paper it reacts in the form of SCl·SCl, the dithio-ketones and the disulphides would have the formulæ $\overset{S}{\underset{S}{|}}{>}C(CO{\cdot}NHPh)_2$ and $\begin{matrix} S{\cdot}CH(CO{\cdot}NHPh)_2 \\ | \\ S{\cdot}CH(CO{\cdot}NHPh)_2 \end{matrix}$ respectively, and compounds of the latter type, for example, dithiosalicyclic acid (Friedländer), are known to have a high order of stability. These questions will form the subject of further investigation.

Experimental.

Dithiomesoxanilide (III).

Nine grams of malonanilide and 10 grams of sulphur monochloride (S_2Cl_2) were heated under reflux with 50 c.c. of dry benzene. As soon as the benzene began to boil, hydrogen chloride gas was vigorously evolved. After three hours the evolution ceased and the product was filtered and washed thoroughly with dry benzene to free it from the excess of sulphur monochloride. The solid residue, which was almost pure and appeared to be free from any precipitated sulphur, was difficultly soluble in acetone, from which it crystallised in short, colourless needles, m. p. 214—215° (Found : N = 8·70 ; S = 20·10. $C_{15}H_{12}O_2N_2S_2$ requires N = 8·86 ; S = 20·25 per cent.).

Two grams of this substance were boiled under reflux with a large quantity of absolute alcohol for two hours in order to determine whether either of the sulphur atoms was separable. The solid, after filtration, was repeatedly extracted with carbon disulphide (Found: N = 9·12; S = 20·33 per cent.

In order to see if the reaction took place in two stages, only half the quantity of sulphur chloride theoretically required was added to malonanilide and the condensation allowed to take place under the same conditions as before. The product was repeatedly boiled with alcohol to free it from any unchanged malonanilide. Almost one-half of the malonanilide was recovered and the other half was completely converted into a dithio-ketone. Thus the reaction appears to take place in one stage only, the substance $[CH(CO{\cdot}NHPh)_2]S_2$ not being formed.

Nitration of Dithiomesoxanilide.—A very vigorous reaction occurred when 5 grams of the anilide were treated with nitric acid (D 1·5), and the whole of the substance dissolved. The nitrated product slowly separated in fine crystals on further warming. It was collected, washed with concentrated nitric acid and with water, and dried, and then melted at 232—233° (Found: N = 16·72; S = 12·60. $C_{15}H_8O_{10}N_6S_2$ requires N = 16·93; S = 12·90 per cent.).

Hydrolysis of Dithiomesoxanilide.—The anilide (15 grams) was hydrolysed by boiling for two hours under reflux with a solution of potassium hydroxide (10 grams) in water (16 grams). The aniline produced by the hydrolysis was extracted with ether and identified. From the aqueous solution a solid was isolated which reacted with hydrochloric acid to produce hydrogen sulphide, and was evidently potassium sulphide which had been formed during the hydrolysis.

Bromination.—Ten grams of dithiomesoxanilide (1 mol.) were treated with bromine (rather more than 3 mols.) in glacial acetic acid solution. The product, after spontaneous evaporation of the acetic acid, smelt of sulphur bromide. When the smell became faint the product was boiled with alcohol under reflux. The solution deposited on cooling light, white tufts, which melted sharply at 239° after repeated crystallisation. The substance was found to be identical with the tribromomalonanilide prepared by the direct bromination of malonanilide (Backes, West, and Whiteley, this vol., p. 373).

Reduction of Dithiomesoxanilide.—Malonanilide, m. p. 224—225°, was produced when dithiomesoxanilide (10 grams), dissolved in boiling alcohol (100 c.c.), was reduced by an alkaline solution of sodium sulphide by Brand's method (*Ber.*, 1909, **42**, 3464).

Dithiomesoxodimethylamide (IV).

This substance, prepared from malondimethylamide (1·5 grams) and sulphur monochloride (about 2 grams) in the same way as dithiomesoxanilide, was difficultly soluble in absolute alcohol. It separated from a concentrated solution in slender needles and ultimately as a crystalline powder which melted at 216—217° (Found: N = 14·24; S = 33·24. $C_5H_8O_2N_2S_2$ requires N = 14·58; S = 33·33 per cent.).

Dithiomesoxodibenzylamide (V).

This substance was prepared from 4 grams of malondibenzylamide and 2 grams of sulphur chloride. The product was dissolved in absolute alcohol, from which it separated in fine, white crystals melting at 204° (Found: N = 8·57; S = 18·18. $C_{17}H_{16}O_2N_2S_2$ *requires* N = 8·34; S = 18·61 *per cent.*).

Malondimethylanilide Disulphide (VIII).

A mixture of 5 grams of malondimethylanilide, 50 grams of dry benzene, and 2·7 grams of sulphur chloride was heated under reflux for three hours. The action was not so vigorous as in the case of malonanilide. The product was washed with dry benzene to remove the unchanged sulphur monochloride, dissolved in hot acetic acid, and precipitated from the solution by hot water. This treatment was repeated until the substance had a constant melting point, 218—219° (Found: S = 10·52. $C_{34}H_{34}O_4N_4S_2$ requires S = 10·22 per cent.).

Methylmalonanilide Disulphide (VII).

Methylmalonanilide was prepared by heating a mixture of methyl methylmalonate (17 grams) and aniline (19 grams) for five hours at 140° and finally at 150—160° until the distillation of methyl alcohol ceased. After crystallisation from alcohol the product melted at 180°.

A mixture of 10 grams of methylmalonanilide, 100 c.c. of dry benzene, and 5 grams of sulphur monochloride was heated under reflux. Evolution of hydrogen chloride began to take place at once. After three hours, the solid was collected, washed with dry benzene, and crystallised from absolute alcohol, when it was obtained as a crystalline powder melting at 229—230° (Found: S = 11·01. $C_{32}H_{30}O_4N_4S_2$ requires S = 10·70 per cent.).

5-Disulphido-1 : 3-diphenylbarbituric acid (XI).

Sulphur monochloride (2·7 grams) dissolved in a small quantity of benzene was gradually added to a boiling mixture of benzene (50 c.c.) and diphenylbarbituric acid (5·6 grams). The acid, which was not soluble in benzene, rapidly disappeared and hydrogen chloride was evolved. After two hours, the brown liquid was cooled and filtered, and the solvent allowed to evaporate. The residue was again dissolved in benzene and, after the solvent had evaporated, crystallised from a mixture of benzene and light petroleum, when it melted sharply at 181°. The molecular weight, determined by the cryoscopic method in benzene solution, was 355·5 (Found: S = 19·20. $C_{16}H_{10}O_3N_2S_2$ requires S = 18·72 per cent.; M = 342).

In conclusion, I take this opportunity of expressing my sincere gratitude to Prof. J. F. Thorpe and Dr. M. A. Whiteley for the keen interest they have shown and the kind encouragement they have given me throughout this work. I also express my thanks to the Chemical Society for a grant from their Research Fund, which has partly defrayed the expenses incurred in this investigation.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, December 31st*, 1920.

XLVI.—*Complex Metallic Ammines. Part V.* cis-*Succinatodiethylenediaminecobaltic Salts, and other Cobaltammine Salts containing a Seven-membered Ring in the Complex.*

By JAMES COOPER DUFF.

WERNER (*Annalen*, 1911, **386**, 79) has obtained *cis*-malonato-salts of the type

$$\left[CH_2{<}{}^{CO\cdot O}_{CO\cdot O}{>}Co\ en_2 \right]X,$$

containing a six-membered ring. He failed to obtain crystalline salts containing an additional carbon atom in the ring when he used succinic, malic, and tartaric acids. He also found (*loc. cit.*, p. 27) that the alkylenediamines can only be used to prepare crystalline metallic ammines when forming a ring of not more than five

or six members with the cobalt atom. The maximum number of atoms in each ring system need not be the same, however, as oxygen atoms are exclusive to one type of ring system, and nitrogen atoms to the other.

Price and Brazier (T., 1915, **107**, 1373), by introducing sulphur into the carbon chain, have obtained an eight-membered ring in salts of the type

$$\left[SO_2<{CH_2\cdot CO\cdot O \atop CH_2\cdot CO\cdot O}>Co\ en_2\right]X.$$

It was therefore thought that the reaction of succinic acid, and similar acids, with carbonatodiethylenediaminecobaltic salts should be further investigated.

Werner has characterised compounds obtained from dibasic acids, like oxalic and malonic acids, as *cis*-compounds (*Annalen*, 1911, **386**, 10). Malic and tartaric acids, in which the carboxyl groups are averted from each other, are not suitable acids for the formation of rings with the cobalt atom in the complex. Succinic acid, although it can form an anhydride, is regarded as having a configuration similar to that of fumaric acid (Bruni, *Atti R. Accad. Lincei*, 1904, [v], **13**, i., 626). Price and Brazier (T., 1915, **107**, 1719) consider that the hydroxyl groups at least must be averted from each other. As will be shown later, the reaction of succinic acid with carbonatodiethylenediaminecobaltic bromide is very similar to that of fumaric acid and different from that of all the other acids examined. Succinic anhydride behaves differently from succinic acid and readily gives the various succinato-salts. In the experimental part it will be seen, however, that succinic acid can be used to produce the hydrogen succinate,

$$\left[{CH_2\cdot CO\cdot O \atop CH_2\cdot CO\cdot O}>Co\ en_2\right]CO_2\cdot CH_2\cdot CH_2\cdot CO_2H,$$

in a crystalline form. The conditions of the preparation suggest that at the higher temperatures used the hydroxyl groups in succinic acid become more labile and render the molecule more suitable for entering into ring-formation.

Mesotartaric, maleic, dibromosuccinic, itaconic, and citraconic acids, in which the carboxyl groups are in the *cis*-position, all give crystalline cobaltammine salts of the desired type.

Tartaric, malic, and mesaconic acids produce viscid syrups which can not be made to solidify. Fumaric acid, though giving no crystalline salts, behaves in an exceptional manner. In these four acids the carboxyl groups are averted from each other. The results prove that only when the carboxyl groups are in the *cis*-position can a seven-membered ring be obtained in the complex.

The preparations were made in the manner described in Part IV (T., 1920, **117**, 1072), and the bromides were proved not to be diaquo-salts by the method set forth in Part I (T., 1915, **107**, 1370).

EXPERIMENTAL.

cis-*Succinatodiethylenediaminecobaltic Salts*, YX, where

$$Y = \left[\begin{matrix} CH_2\cdot CO\cdot O \\ CH_2\cdot CO\cdot O \end{matrix} > Co\ en_2 \right].$$

The *bromide*, $YBr,2H_2O$, separated in minute, brownish-red plates when 1·6 grams of succinic anhydride were added to a boiling solution of 5 grams of carbonatodiethylenediaminecobaltic bromide in 100 c.c. of water, and the solution, after being boiled for two minutes, was concentrated to a small bulk and left in the ice chest (Found: Co = 14·31; Br = 19·27; H_2O = 8·83. $C_8H_{20}O_4N_4BrCo,2H_2O$ requires Co = 14·35; Br = 19·45; H_2O = 8·76 per cent.).

The foregoing product was not obtained in crystalline form by the interaction of succinic acid and the carbonato-bromide in boiling solution, or even at 105° under pressure. Concentration and subsequent cooling led to a clear, red jelly which readily formed a red powder when stirred with alcohol. This powder only formed the jelly-like product when it was redissolved in water, although its properties corresponded with those of the succinato-bromide.

The *nitrate*, $YNO_3,2H_2O$, was obtained in microscopic, brownish-red, elongated plates by precipitating a solution of 3 grams of the bromide with 1·24 grams of silver nitrate, and concentrating the filtrate to a small bulk (Found: Co = 14·84; N = 17·66; H_2O= 9·34. $C_8H_{20}O_4N_5Co,2H_2O$ requires Co = 15·01; N = 17·85; H_2O = 9·16 per cent.).

The *hydrogen succinate*, $Y\cdot CO_2\cdot CH_2\cdot CH_2\cdot CO_2H,4H_2O$, was obtained by adding 4·44 grams of succinic acid to a boiling solution of the carbonato-base prepared from 6 grams of the carbonato-bromide in 120 c.c. of water and 4 grams of freshly prepared, moist silver oxide. The resulting solution, after being boiled for five minutes, was evaporated to low bulk and a little alcohol stirred in. The product was obtained in microscopic crystals, and after recrystallisation from water in brownish-red, elongated plates. The yield was 4·25 grams (Found: Co = 12·07; N = 11·73; H_2O = 14·83. $C_{12}H_{25}O_8N_4Co,4H_2O$ requires Co = 12·18; N = 11·57; H_2O = 14·87 per cent.).

The presence of some succinato-bromide in the amorphous powder obtained by the action of succinic acid on the carbonato-bromide was proved by converting it into the hydroxide by shaking in solution with moist silver oxide and adding a molecular equivalent

of succinic acid to the filtrate. On evaporation, brownish-red plates of the hydrogen succinate were obtained. (Found: Co = 12·47; H_2O = 14·62 per cent.).

cis-*Maleatodiethylenediaminecobaltic Salts*, YX, where

$$Y = \left[\begin{matrix}CH\cdot CO\cdot O \\ CH\cdot CO\cdot O\end{matrix}\!\!>Co\ en_2\right].$$

The *bromide*, $YBr,2H_2O$, was obtained in minute, brownish-red crystals by adding 1·82 grams of maleic acid to a hot solution of 5 grams of the carbonato-bromide in 100 c.c. of water, boiling for five minutes and then evaporating to low bulk (Found: Co = 14·55; Br = 19·83; H_2O = 8·89. $C_8H_{18}O_4N_4BrCo,2H_2O$ requires Co = 14·45; Br = 19·54; H_2O = 8·80 per cent.).

The bromide in aqueous solution does not give a precipitate with a solution of barium hydroxide. This indicates that all the maleato-radicle is in the complex.

The *nitrate*, YNO_3,H_2O, was obtained in minute, brownish-red crystals from the bromide in the same way as the succinato-nitrate (Found: Co = 15·91; N = 18·59; H_2O = 4·62. $C_8H_{18}O_7N_5Co,H_2O$ requires Co = 15·81; N = 18·76; H_2O = 4·82 per cent.).

The *hydrogen maleate*, $Y\cdot CO_2\cdot CH{:}CH\cdot CO_2H$, was obtained in minute, pink, flattened needles in the same way as the corresponding succinato-salt (Found: Co = 14·55; N = 13·88. $C_{12}H_{21}O_8N_4Co$ requires Co = 14·45; N = 13·72 per cent.). An aqueous solution of the salt gives a white precipitate with a solution of barium hydroxide, indicating that the salt is a maleate.

cis-*Mesotartratodiethylenediaminecobaltic Salts*, YX, where

$$Y = \left[\begin{matrix}HO\cdot CH\cdot CO\cdot O \\ HO\cdot CH\cdot CO\cdot O\end{matrix}\!\!>Co\ en_2\right].$$

The *bromide*, $YBr,2H_2O$, was prepared in the same way as the maleato-bromide from 1·41 grams of mesotartaric acid and 3 grams of the carbonato-bromide, and was obtained in minute, brownish-red crystals (Found: Co = 13·12; Br = 17·80; H_2O = 8·26. $C_8H_{20}O_6N_4BrCo,2H_2O$ requires Co = 13·31; Br = 18·03; H_2O = 8·13 per cent.).

The *hydrogen mesotartrate*, $Y\cdot CO_2\cdot CH(OH)\cdot CH(OH)\cdot CO_2H,H_2O$ was obtained in minute, pink crystals from two molecular proportions of mesotartaric acid and one of the carbonato-hydroxide in the usual way (Found: Co = 11·80; N = 11·44; H_2O = 3·74. $C_{12}H_{25}O_{12}N_4Co,H_2O$ requires Co = 11·94; N = 11·33; H_2O = 3·64 per cent.).

cis-*Dibromosuccinatodiethylenediaminecobaltic Salts*, YX, where

$$Y = \left[\begin{matrix}CHBr\cdot CO\cdot O \\ CHBr\cdot CO\cdot O\end{matrix}>Co\ en_2\right].$$

The *bromide*, $YBr,2H_2O$, was obtained in minute, purplish-red crystals by stirring 4·32 grams of dibromosuccinic acid into a boiling solution of 5 grams of the carbonato-bromide in 120 c.c. of water and evaporating the solution at 60° under diminished pressure to prevent hydrolysis of the dibromosuccinic acid (Found: Co = 10·25; N = 10·28; H_2O = 6·49. $C_8H_{18}O_4N_4Br_3Co,2H_2O$ requires Co = 10·36; N = 9·84; H_2O = 6·33 per cent.).

The *nitrate*, YNO_3, was obtained in purplish-pink, minute crystals from the bromide and silver nitrate (Found: Co = 11·62; N = 13·66. $C_8H_{18}O_7N_5Br_2Co$ requires Co = 11·45; N = 13·59 per cent.).

The *normal dibromosuccinate*, $Y\cdot CO_2\cdot CHBr\cdot CHBr\cdot CO_2\cdot Y$, was obtained in the attempt to prepare the hydrogen dibromosuccinate from two molecular proportions of the acid and one of the carbonato-base. Evaporation under diminished pressure and addition of alcohol caused the normal salt to separate in pale mauve, minute crystals (Found: Co = 10·15; N = 9·83; Br = 39·72. $C_{20}H_{38}O_{12}N_8Br_6Co_2$ requires Co = 10·00; N = 9·50; Br = 40·05 per cent.).

cis-*Itaconatodiethylenediaminecobaltic Hydrogen Itaconate*,

$$\left[\begin{matrix}CH_2{:}C\cdot CO\cdot O \\ \quad CH_2\cdot CO\cdot O\end{matrix}>Co\ en_2\right]CO_2\cdot C_3H_4\cdot CO_2H,5H_2O.$$

This, the only salt prepared from itaconic acid, was obtained in the same way as the succinato-hydrogen succinate, from itaconic acid (2 mols.) and the carbonato-base (1 mol.). The salt crystallised in brownish-red, flattened needles (Found: Co = 11·06; N = 10·47; H_2O = 17·04. $C_{14}H_{25}O_8N_4Co,5H_2O$ requires Co = 11·17; N = 10·64; H_2O = 16·92 per cent.).

cis-*Citraconatodiethylenediamine Hydrogen Citraconate*,

$$\left[\begin{matrix}CMe\cdot CO\cdot O \\ CH\cdot CO\cdot O\end{matrix}>Co\ en_2\right]CO_2\cdot C_3H_4\cdot CO_2H,$$

was obtained in minute, pink needles, prepared in the same way as the last-mentioned compound (Found: Co = 13·39; N = 12·71. $C_{14}H_{25}O_8N_4Co$ requires Co = 13·53; N = 12·84 per cent.).

The use of fumaric acid in the same way as that of maleic acid in attempts to prepare the bromide, nitrate, and hydrogen fumarate respectively, led in each case to a clear, red jelly, which gave a

quantitative yield of pink, amorphous powder when stirred with an excess of alcohol. The respective powders could not be crystallised from water. The analyses and reactions corresponded with those of the expected salts, but the substances were apparently of a more complex nature.

Mesaconic acid used in the same way as fumaric acid produced only non-crystallisable syrups similar to those obtained with tartaric and malic acids.

All the bromides described gave pink, amorphous precipitates of indefinite composition with mercuric bromide in potassium bromide solution. With chloroplatinic acid the bromides and nitrates gave brownish-pink precipitates.

Many cobaltammine salts containing the radicle of a dibasic acid in the complex have now been prepared. The influence of the various acid radicles on certain physical properties of the salts will be described later. The introduction of radicles of dibasic, aromatic acids is now under investigation.

The author's thanks are due to Dr. T. Slater Price for facilities which have made this work possible.

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[*Received, February* 3*rd*, 1921.]

XLVII.—*Compounds of Hexamethylenetetramine with Complex Metallic Salts and Acids.*

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SEVERAL workers have already shown that hexamethylenetetramine combines with various metallic salts to form molecular or additive compounds similar to those formed by ammonia (Partesi, *Gazzetta*, 1883, **13**, 437; Moschatos and Tollens, *Ber.*, 1891, **24**, 695; *Annalen*, 1893, **272**, 271; Ley, *Annalen*, 1894, **278**, 57; *Compt. rend.*, 1894, **119**, 1211; 1895, **120**, 743; Schwartz, *Chem. Zeit.*, 1890, **14**, 787; Hofmann, *Ber.*, 1906, **39**, 3181; Bergell, *Deut. med. Woch.*, 1907, **33**, 55; Schmiz, *Ber. Deut. pharm. Ges.*, 1910, **20**, 201; Calzolari, *Ber.*, 1910, **43**, 2217; Barbieri and Calzolari, *Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 584; 1911, [v], **20**, ii, 119, 161; *Zeitsch. anorg. Chem.*, 1911, **71**, 347; Scagliarini, *Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 151, 642; Calzolari, *ibid.*, 1913, [v], **22**, i, 787; Barbieri,

ibid., 1914, [v], **23**, ii, 8; Rossi, *Gazzetta*, 1913, **43**, ii, 669; Scagliarini and Rossi, *Atti R. Accad. Lincei*, 1913, [v], **25**, ii, 506; Vanino and Sachs, *Arch. Pharm.*, 1913, **25**, i, 292; Calzolari and Tagliavini, *Atti R. Accad. Lincei*, 1915, [v], **24**, i, 925; Vanino and Schinner, *Arch. Pharm.*, 1914, **252**, 449; Scagliarini and Marangoni, *Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 1214). In the present paper compounds of hexamethylenetetramine with complex metallic salts and acids are described. All these compounds are more or less soluble in water, the compounds with acids being much less soluble than those with salts.

They are all beautifully crystalline, additive compounds, which decompose in solution into their constituents. The additive nature of these compounds has been conclusively proved by determining the molecular conductivities in certain cases.

The compounds with complex acids have the compositions given in the experimental portion of this paper; they should be viewed as simple, molecular compounds and not as the acid salts of hexamethylenetetramine, because the latter are not likely to be formed by such a very weak base. Wagener and Tollens (*Ber.*, 1906, **39**, 410) have described compounds of hydroferro-, hydroferri-, and hydrocobalti-cyanic acids with hexamethylenetetramine of the general composition $A,2B,xH_2O$. Although the methods of preparation are very similar to those employed by us, it cannot be definitely stated whether these different results are due to the actual existence of different compounds under different conditions or to the impurities which they admitted were present in their preparations.

Another series of compounds has been obtained, which may be classified with the above series as molecular compounds of hexamethylenetetramine with mineral acids, or unstable, complex metallic acids and metallic salts, or as compounds of hexamethylenetetramine salts of complex or simple acids, metallic salts, and free hexamethylenetetramine. Similar cases, in which unstable, complex metallic acids were stabilised by hexamethylenetetramine, have already been described by previous workers. Their compositions are represented by the following formulæ:

$2CdI_2,2HI,3C_6H_{12}N_4$ or $CdI_2,H_2CdI_4,3C_6H_{12}N_4$.

$2HgI_2,2HI,3C_6H_{12}N_4$ or $HgI_2,H_2HgI_4,3C_6H_{12}N_4$.

$2Cr(SCN)_3,3HSCN,5C_6H_{12}N_4$ or $H_3Cr(SCN)_6,Cr(SCN)_3,5C_6H_{12}N_4$.

$SnCl_2,HCl,C_6H_{12}N_4$ or $SnCl_2,H_2SnCl_4,2C_6H_{12}N_4$.

$2SnCl_4,HCl,3C_6H_{12}N_4,4H_2O$ or $3SnCl_4,H_2SnCl_6,6C_6H_{12}N_4,8H_2O$.

A similar compound is also formed with chloroplumbic acid, but as it readily decomposes the composition cannot be determined.

EXPERIMENTAL.

Compounds of Hexamethylenetetramine.

With Sodium Nitroprusside.—Pale brown crystals of the double compound separated at once when concentrated solutions of sodium nitroprusside and hexamethylenetetramine were mixed. They were drained, washed with a little water and with alcohol, and dried in the air or in a vacuum over sulphuric acid. They were readily soluble in water, giving a brownish-red solution.

Iron was estimated as ferric oxide after the substance had been heated with concentrated sulphuric acid. Hexamethylenetetramine was estimated, after the complex acid had been precipitated as the cadmium salt by the addition of a concentrated solution of cadmium sulphate and the filtrate had been evaporated to dryness on the water-bath, by adding standard sulphuric acid and titrating the excess with standard alkali (compare Base, *Pharm. Zeit.*, 1907, **52**, 851) (Found: Fe = 9·2, 9·2; $C_6H_{12}N_4$ = 24·4, 24·5. $Na_2Fe(CN)_5(NO),C_6H_{12}N_4,11H_2O$ requires Fe = 9·3; $C_6H_{12}N_4$ = 23·3 per cent.).

With Potassium Ferricyanide.—This compound was obtained as a golden-yellow, crystalline precipitate when a saturated solution of potassium ferricyanide was mixed with a saturated solution of hexamethylenetetramine. It was dried and analysed as described above (Found: Fe = 9·0, 9·05; $C_6H_{12}N_4$ = 21·6, 21·4. $K_3Fe(CN)_6,C_6H_{12}N_4,9H_2O$ requires Fe = 8·9; $C_6H_{12}N_4$ = 22·2 per cent.).

Action of Hexamethylenetetramine on Potassium Ferrocyanide.—When a saturated solution of potassium ferrocyanide was mixed with a saturated solution of hexamethylenetetramine, a pale lemon-yellow, crystalline precipitate was formed, which proved to be partly dehydrated potassium ferrocyanide (Found: Fe = 14·3. $K_4Fe(CN)_6,1\frac{1}{2}H_2O$ requires Fe = 14·18 per cent.).

With Potassium Cobalticyanide.—Saturated solutions of potassium cobalticyanide and hexamethylenetetramine, on being mixed together, gave a white, crystalline precipitate (Found: Co = 10·1, 10·2; $C_6H_{12}N_4$ = 23·0, 23·2. $K_3Co(CN)_6,C_6H_{12}N_4,6\frac{1}{2}H_2O$ requires Co = 10·01; $C_6H_{12}N_4$ = 23·76 per cent.).

With Potassium Chromicyanide.—A very pale-brown precipitate was obtained when saturated solutions of hexamethylenetetramine and potassium chromicyanide were mixed. The product was of indefinite composition. It contained chromicyanidion as well as hexamethylenetetramine, and was probably a mixture of different compounds.

Action of Hexamethylenetetramine on Sodium Cobaltinitrite.—When

a solution of the base was added to a solution of sodium cobaltinitrite, a deep yellow precipitate was formed, which was very sparingly soluble in water and was easily decomposed by dilute acids. From the analysis of the compound (Found: Co = 10·5, Na = 4·0, C = 19·15, H = 4·8, N = 25·3. The formula requires Co = 10·4, Na = 4·1, N = 24·7, C = 19·0, and H = 5·1 per cent.) it would appear that in the presence of hexamethylenetetramine sodium cobaltinitrite was first converted into sodium tetranitritodiaquocobaltate, which then combined with hexamethylenetetramine to form the sparingly soluble compound. The reactions may be represented by the equations:

$$Na_3[Co(NO_2)_6] + 2H_2O = Na[Co(NO_2)_4(H_2O)_2] + 2NaNO_2$$
$$2Na[Co(NO_2)_4(H_2O)_2] + 3C_6H_{12}N_4 + 6H_2O$$
$$= 2Na[Co(NO_2)_4(H_2O)_2],3C_6H_{12}N_4,6H_2O.$$

With Cadmium Iodide.—When concentrated solutions of cadmium iodide (or of cadmium sulphate and potassium iodide) and hexamethylenetetramine were mixed, a white, crystalline precipitate of the double compound was formed (Found: Cd = 23·8; $C_6H_{12}N_4$ [by combustion] = 20·2. $3CdI_2,2C_6H_{12}N_4$ requires Cd = 24·3; $C_6H_{12}N_4$ = 20·3 per cent.).

With Hydroferrocyanic Acid.—A white, crystalline precipitate was obtained by mixing solutions of hexamethylenetetramine and freshly prepared hydroferrocyanic acid or potassium ferrocyanide (in the latter case the mixture was acidified). When perfectly dry, the compound was moderately stable, but in moist air it gradually developed a faintly yellow tint and after some days became green, owing to slow decomposition and the formation of Prussian blue. In the presence of an excess of hexamethylenetetramine, however, it dissolved, forming a slightly yellow solution, the colour of which intensified on keeping. When the solution was evaporated in a vacuum over sulphuric acid, lemon-yellow crystals of a second compound were obtained. The substance was moderately stable.

Hexamethylenetetramine was estimated as in the case of the sodium nitroprusside and the potassium ferrocyanide compounds, but in this case the amount of free acid liberated by hydroferrocyanic acid from cadmium sulphate had to be taken into consideration in calculating the percentage of hexamethylenetetramine. This amount was known from the percentage of iron. The result was confirmed by the estimation of nitrogen by Dumas's method (Found for the white compound: Fe = 11·7; $C_6H_{12}N_4$ = 37·5. $3H_4Fe(CN)_6,4C_6H_{12}N_4,13H_2O$ requires Fe = 11·66; $C_6H_{12}N_4$ = 38·8 per cent. Found for the yellow compound: Fe = 11·7;

$C_6H_{12}N_4$ = 49·4. $3H_4Fe(CN)_6,5C_6H_{12}N_4,4\frac{1}{2}H_2O$ requires Fe = 11·75; $C_6H_{12}N_4$ = 49·0 per cent.).

With Hydroferricyanic Acid.—Solutions of potassium ferricyanide and hexamethylenetetramine were mixed and acidified with dilute hydrochloric acid, when bright yellow crystals were deposited. The compound was moderately stable in the dry state, but decomposed slowly on keeping, Prussian blue being formed and hydrogen cyanide evolved (Found: Fe = 11·2, 11·2; $C_6H_{12}N_4$ = 36·9. $3H_3Fe(CN)_6,4C_6H_{12}N_4,16H_2O$ requires Fe = 11·25; $C_6H_{12}N_4$ = 37·5 per cent.).

With Hydrocobalticyanic Acid.—This compound was prepared from potassium cobalticyanide in a similar way. The white, crystalline substance obtained was quite stable in the dry state (Found: Co = 12·6; $C_6H_{12}N_4$ = 42·3. $3H_3Co(CN)_6,4C_6H_{12}N_4,9H_2O$ requires Co = 12·86; $C_6H_{12}N_4$ = 40·0 per cent.).

With Cadmium Iodide and Hydriodic Acid.—To a solution containing cadmium iodide and potassium iodide, a solution of hexamethylenetetramine was added. No precipitation occurred at the dilution employed, but on acidifying with dilute hydrochloric acid a white, crystalline precipitate was obtained (Found: Cd = 16·00: I = 54·30; $C_6H_{12}N_4$ [by combustion] = 30·65. $2CdI_2,2HI,3C_6H_{12}N_4$ requires Cd = 15·91; I = 54·12; $C_6H_{12}N_4$ = 29·82 per cent.).

With Mercuric Iodide and Hydriodic Acid.—This compound was prepared from mercuric iodide in a similar way, when a lemon-yellow, crystalline precipitate was obtained after the addition of hydrochloric acid (Found: Hg = 25·03; I = 48·00; $C_6H_{12}N_4$ [by combustion] = 26·5. $2HgI_2,2HI,3C_6H_{12}N_4$ requires Hg = 25·25; I = 48·1; $C_6H_{12}N_4$ = 26·51 per cent.).

With Chromic Thiocyanate and Thiocyanic Acid.—A solution of hexamethylenetetramine was mixed with a solution of potassium chromithiocyanate. On acidifying with dilute hydrochloric acid an amethyst-violet, crystalline precipitate was obtained. The substance gradually decomposed on keeping (Found: Cr = 7·92; SCN = 38·9; $C_6H_{12}N_4$ [by combustion] = 50·4. $2Cr(SCN)_3,3HSCN,5C_6H_{12}N_4$ requires Cr = 7·82; SCN = 39·2; $C_6H_{12}N_4$ = 52·67 per cent.).

With Stannous Chloride and Hydrochloric Acid.—This compound was obtained as a white precipitate when a solution of hexamethylenetetramine was added to a solution of stannous chloride and hydrochloric acid (Found: Sn = 32·1, 32·2; Cl = 28·45; $C_6H_{12}N_4$ [by combustion] = 37·52. $SnCl_2,HCl,C_6H_{12}N_4$ requires Sn = 32·47; Cl = 29·00; $C_6H_{12}N_4$ = 38·2 per cent.).

With Stannic Chloride and Hydrochloric Acid.—A white, crystalline precipitate was obtained from stannic chloride in a similar manner

(Found: Sn = 23·01; Cl = 30·1; $C_6H_{12}N_4$ [by combustion] = 40·1. $2SnCl_4,HCl,3C_6H_{12}N_4,4H_2O$ requires Sn = 22·8; Cl = 30·04; $C_6H_{12}N_4$ = 40·0 per cent.).

With Tetrathiocyanatodiamminechromic Acid.—To a solution of Morland's salt (ammonium tetrathiocyanatodiamminechromate) acidified with dilute hydrochloric acid a solution of hexamethylenetetramine was added. A pale rose, crystalline precipitate was obtained (Found: Cr = 12·1, 12·1; S = 29·4; N = 29·0; C = 23·3. $4H[Cr(SCN)_4(NH_3)_2],3C_6H_{12}N_4$ requires Cr = 12·2; N = 29·7; C = 24·0; N = 29·4 per cent.).

The same compound was also obtained without the addition of hydrochloric acid; in this case ammonia was liberated from the solution.

A golden-yellow, crystalline compound,

$$4H[Co(NO_2)_4(NH_3)_2],3C_6H_{12}N_4,$$

analogous to the preceding, was prepared from tetranitrodiamminecobaltic acid and hexamethylenetetramine.

Conductivity Measurements.

The electrical conductivities of hexamethylenetetramine and of the compounds described above were measured in aqueous solution.

Cell constant = 0·167.

Name	Molecular *dilution*, in litres	μ_v	Temp.
Hexamethylenetetramine	—	negligible	25·8°
Potassium cobalticyanide compound	999	370·8	25·35
Hydrocobalticyanic acid compound	1049	922	25·35
Sodium nitroprusside compound	1385	236	25·8
Potassium ferricyanide compound	592	421	25·05
,, ,, ,,	1184	460·2	26·3
Hydroferricyanic acid compound	1380	1098	25·7
Hydroferricyanic acid compound (white salt)	192	801·6	24·9
Hydroferricyanic acid compound (white salt)	384	963·4	,,
Hydroferricyanic acid compound (white salt)	768	1140	,,
Hydroferrocyanic acid compound (yellow salt)	224	679·2	25
Hydroferrocyanic acid compound (yellow salt)	448	814·8	,,
Hydroferrocyanic acid compound (yellow salt)	896	957·5	,,
Hydroferrocyanic acid compound (yellow salt)	1792	1137·0	,,

At 25°, the equivalent conductivity of sodium nitroprusside is 109·3 (v = 1024), and of potassium ferricyanide 158·6 (v = 512) and 163·6 (v = 1024). A comparison of these values with the

molecular conductivities recorded in the table shows that the compounds of hexamethylenetetramine with sodium nitroprusside and with potassium ferricyanide respectively must have the compositions given to them, because the molecular conductivities agree moderately well with those of the free salts, the compounds being completely broken up into their components in aqueous solution. In the case of the two compounds with hydroferrocyanic acid (containing $3H_4Fe[CN]_6$), the molecular dilution must be divided by 3, and the molecular conductivity at the corrected dilution compared with the molecular conductivity of the free acid at the corresponding dilution. The values thus deduced agree moderately well with the known values for the free acid ($\mu_{64} = 1000$; $\mu_{128} = 1064$; $\mu_{256} = 1134$; $\mu_{512} = 1214$; $\mu_{1024} = 1301$, at 25°).

The molecular conductivities of hydroferricyanic acid are not known, as the acid is very unstable, but the approximate magnitudes may be deduced from the values of the molecular conductivities of its compound with hexamethylenetetramine.

Our best thanks are due to Prof. Sir P. C. Rây for his kind encouragement.

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XLVIII.—*The Interaction of Sulphur Monochloride and Substituted Ethylenes.*

By William Jackson Pope and James Leonard Brierley Smith.

Since it has been shown (Gibson and Pope, T., 1920, **117**, 271) that ethylene is absorbed by sulphur monochloride with production of ββ′-dichlorodiethyl sulphide in accordance with the equation:

$$2CH_2{:}CH_2+S_2Cl_2=(CH_2Cl\cdot CH_2)_2S+S,$$

it became desirable to ascertain whether a similar reaction occurred with derivatives of ethylene. Sulphur monochloride, purified by distillation with sulphur and absorbent charcoal under 11 mm. pressure, was found not to act upon trichloroethylene on prolonged boiling; on heating the mixture in a sealed tube at 140—150° for some hours a clear, yellow liquid was obtained which soon deposited crystalline sulphur, and on distillation yielded a few drops of an evil-smelling, red oil and a large amount of pentachloroethane boiling at 160°. Sulphur monochloride thus acts merely as a chlorinating agent on trichloroethylene.

The homologues of ethylene, propylene, and β-butylene, were found to act upon sulphur monochloride in precisely the same manner as does ethylene itself; it is thus shown that the equation given above represents a general reaction of the ethylenic hydrocarbons.

Experimental.

ββ′-*Dichlorodipropyl Sulphide*, $(CHMeCl{\cdot}CH_2)_2S$.

Sulphur monochloride is introduced into a series of absorption bulbs, which can be vigorously shaken by mechanical means, immersed in a water-bath for the purpose of regulating the temperature. Carefully dried propylene, prepared by the action of *n*-propyl alcohol on phosphoric acid in the manner described by Newth (T., 1901, **79**, 915), is then passed through the bulbs at such a speed that some escapes absorption; at temperatures above 30° absorption commences after a short time, and proceeds with increasing speed until a maximum rate is attained. The rate at which propylene is absorbed by sulphur monochloride increases rapidly with rise of temperature; absorption proceeds about twice as fast at 100° as at 60°.

The reaction between propylene and sulphur monochloride is attended by a large evolution of heat which renders necessary very efficient regulation of the temperature; with the apparatus which we employ it is impossible to treat more than 10 grams of sulphur monochloride with propylene at any temperature below 100° without the evolution of torrents of hydrogen chloride and the production of a black, resinous product which gives but a small yield of ββ′-dichlorodi-*n*-propyl sulphide on distillation. The failure of Coffey (this vol., p. 94) to prepare the sulphide by the method now described must be attributed to inefficient temperature control.

When the reaction proceeds below 70° the product is a pale yellow oil from which crystalline sulphur is generally deposited after cooling; when absorption proceeds at 80—100° a dark-coloured oil results, which deposits a large amount of crystalline sulphur on cooling in the absorption bulbs. In either case almost exactly two molecular proportions of propylene are absorbed by each one of sulphur monochloride. It is noteworthy that the catalytic hastening of the absorption of gas by the sulphur monochloride, which Gibson and Pope showed to follow a preliminary addition of ββ′-dichlorodiethyl sulphide, is not observed in the case of propylene; an addition of an already formed reaction product does not influence perceptibly the rate of absorption of propylene.

On distillation under 11 mm. pressure, ββ′-*dichlorodipropyl*

sulphide, $(CHMeCl{\cdot}CH_2)_2S$, passes over at 105—106° as a colourless oil, whilst a dark, viscid liquid remains which consists largely of sulphur; the yield of sulphide is about 80 per cent. of that theoretically possible (Found: C = 38·07; H = 6·38; Cl = 38·13; S = 17·24. $C_6H_{12}Cl_2S$ requires C = 38·50; H = 6·42; Cl = 37·97; S = 17·66 per cent.). Contrary to the statement of Coffey, this substance exerts a considerable vesicant action on the skin; a small drop placed on the forearm caused a painful, red swelling after ten hours and the whole limb became rather painful.

The sulphide is oxidised vigorously by cold nitric acid, and the clear solution deposits an oil on dilution which is probably the sulphoxide; this on heating at 100° with nitric acid is converted into another oily substance, probably the corresponding sulphone, which also refuses to crystallise. On prolonged boiling with 60 per cent. nitric acid the sulphide yields a vapour with the odour of chloropicrin, and when evaporated the residual solution is found to contain sulphuric acid; after treatment with barium carbonate, filtration, and evaporation, a soluble barium salt is obtained which may be purified by crystallisation from water, in which it is very soluble. This compound is *barium β-chloropropanesulphonate*, $(CHMeCl{\cdot}CH_2{\cdot}SO_3)_2Ba,2H_2O$, which crystallises in colourless scales (Found: H_2O = 7·07. $C_6H_{12}O_6Cl_2S_2Ba,2H_2O$ requires H_2O = 7·73 per cent. Found in anhydrous salt: Ba = 30·57. $C_6H_{12}O_6Cl_2S_2Ba$ requires Ba = 30·37 per cent.).

ββ′-*Dichlorodi*-sec.-*butyl Sulphide*, $(CHMeCl{\cdot}CHMe)_2S$.

The β-butylene required for the preparation of this compound was made by the action of phosphoric acid on *n*-butyl alcohol as described by King (T., 1919, **115**, 1404), who showed that the product is almost pure β-butylene, CHMe:CHMe. On passing well-dried β-butylene through sulphur monochloride in the manner already described, absorption proceeds with great rapidity; comparative experiments showed that this hydrocarbon is absorbed about ten times as fast as ethylene by sulphur monochloride at 60°. The speed of absorption increases rapidly as the temperature is raised, and proceeds from four to five times as fast at 100° as at 30°. As with propylene, the addition of preformed reaction product to the sulphur monochloride does not appreciably hasten the absorption of the β-butylene.

As in the case of propylene absorption, the reaction is attended by a large heat evolution which renders efficient temperature control essential, and the reaction proves uncontrollable when more

than 10 grams of sulphur chloride are treated in our apparatus with β-butylene at 100°; in this event torrents of hydrogen chloride are evolved, and a black, resinous product results. The most convenient mode of operation consists in starting the absorption at 60° and raising the temperature during one hour to 100°, the gas being passed through at such a rate that some escapes unabsorbed; absorption ceases in about an hour from the commencement. Each molecular proportion of sulphur monochloride absorbs almost exactly two of β-butylene. The product of absorption at 100° is a light brown oil which yields a copious deposit of sulphur on cooling; if the temperature does not rise above 80° during the reaction, a pale yellow oil results, which gives no deposit of sulphur on remaining at the ordinary temperature, although, on heating the oil to 100° and seeding after cooling, some crystalline sulphur is deposited.

When the reaction product is distilled under 11 mm. pressure a pale yellow oil passes over at 120—160° and a dark, viscid resin, consisting mainly of sulphur, remains behind; fractional distillation of the oil under reduced pressure yields *ββ'-dichlorodi*-sec.-*butyl sulphide* as an oil, which has a faint yellow tint and boils at 121—122°/11 mm. The sulphide has a faint odour somewhat recalling that of ββ'-dichlorodiethyl sulphide, and is converted into a white, resinous solid on immersion in liquid air (Found: Cl = 32·85; S = 14·71. $C_8H_{16}Cl_2S$ requires Cl = 33·02; S = 14·89 per cent.). It is almost without vesicant action; a drop left on the back of the hand for eight hours caused no inconvenience, and a little placed under the finger-nail caused only a slight burning sensation after about five hours.

The sulphide is vigorously oxidised by cold nitric acid, but the oil which separates on dilution seems, from analysis, to be a mixture of the corresponding sulphoxide and sulphone; after heating with nitric acid at 100° and evaporating the solution, *ββ'-dichlorodi*-sec.-*butylsulphone*, $(CHMe{\cdot}ClCHMe)_2SO_2$, separates as a colourless, viscous oil which becomes converted into a resinous mass on immersion in boiling liquid air (Found: Cl = 27·31. $C_8H_{16}O_2Cl_2S$ requires Cl = 27·74 per cent.).

On prolonged boiling with 60 per cent. nitric acid the sulphide is oxidised with the evolution of vapours having the odour of chloropicrin; the solution contains sulphuric acid, and, after removing this by treatment with barium carbonate, the filtered solution yields the barium salt of a sulphonic acid, which is extremely soluble in water. On recrystallisation from boiling water this salt is obtained in colourless, crystalline scales, and proves to be *barium β-chlorobutane-γ-sulphonate*,

$$(CHMeCl{\cdot}CHMe{\cdot}SO_3)_2Ba,2H_2O$$

(Found : H_2O = 7·02. $C_8H_{16}O_6Cl_2S_2Ba,2H_2O$ requires H_2O = 6·98 per cent. Found, in anhydrous salt : Ba = 28·91. $C_8H_{16}O_6Cl_2S_2Ba$ requires Ba = 28·60 per cent.).

On boiling the dichlorodi-*sec.*-butyl sulphide for some hours with an alcoholic solution of sodium sulphide and distilling the product in a current of steam, the symmetrical *tetramethyldiethylenedisulphide*, $S<{CHMe\cdot CHMe \atop CHMe\cdot CHMe}>S$, is obtained as a colourless oil with an odour of decaying onions, which boils at 145—150°/35 mm. (Found : S = 37·71. $C_8H_{16}S_2$ requires S = 36·36 per cent.).

It is interesting to notice that ethylene, propylene, and β-butylene react in exactly the same manner with sulphur monochloride, yielding β-chloro-substituted alkyl sulphides, together with sulphur, but that the readiness with which reaction occurs is very different in the three cases. A series of determinations of the speed of absorption of these three hydrocarbons by sulphur monochloride has been made under comparable conditions of rate of stirring, etc.; the following table gives the number of litres of gas, measured at N.T.P., absorbed by 135 grams of sulphur monochloride at 60° :

Time in hours.	Volume absorbed. Ethylene.	Propylene.	β-Butylene.
0·4	—	5·5	26·0
0·8	—	23·0	40·2
1·0	0·3	33·0	42·3
1·5	0·6	43·0	43·2
2·0	1·0	43·8	Ended.
3·0	2·7	Ended.	
4·0	6·7		
5·0	23·0		
6·0	43·8		

It is to be concluded from the work now described that the reaction described by Gibson and Pope is a general reaction of ethylene and its homologues.

THE CHEMICAL LABORATORY,
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XLIX.—*The Binary System, Aniline–acetic Acid.*

By EDMUND ARTHUR O'CONNOR.

No reference can be found to the preparation of any compound of aniline and acetic acid in the solid state. Fehling (*Neues Handwörterbuch der Chemie*, 1, 577) mentions this fact. Tizard (T., 1910, 97, 2493) attempted to prepare a compound by mixing

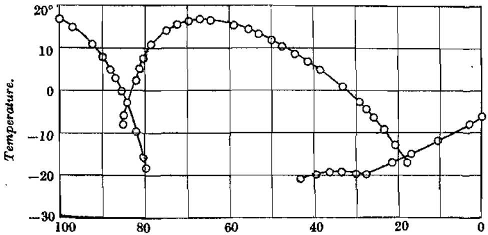
the base and the acid in molecular proportions and cooling the mixture to − 20°. He failed to obtain any solid and concluded that the liquid was supercooled. It seemed worth while, therefore, to investigate fully the binary system, aniline-acetic acid.

EXPERIMENTAL.

The aniline used was a sample prepared from Merck's aniline sulphate, and purified by repeated distillation. Its freezing point was − 6·0°. The acetic acid was purified by fractional freezing until a constant, maximum freezing point of 16·6° was attained.

The apparatus was that usually employed in freezing-point work, with the device described by Beckmann (*Zeitsch. physikal. Chem.*, 1891, **7**, 323) for use with hygroscopic substances of low volatility.

FIG. 1.



Molecular percentage of acetic acid.

In the first experiments the mixtures were made up synthetically and the temperatures of equilibrium between solid and liquid were determined in the usual way. This procedure had to be abandoned with certain mixtures owing to the sluggishness with which the solid and the liquid phases came to equilibrium. The analytical method was substituted, the composition of the liquid in equilibrium with a large quantity of the solid phase at a particular temperature being obtained by removing some of the liquid through a glass-wool filter, and titrating the acetic acid in a weighed quantity of it against standard alkali. The aniline content was obtained by difference. Acetic acid may be titrated without error in presence of aniline. In using this method a sufficiently constant temperature was obtained by immersing the apparatus in a large Dewar flask containing water or a freezing mixture at the required temperature. The results are given in the following table and are

plotted in the figure, a few points being omitted to avoid undue crowding. The data for points in the metastable regions are marked with an asterisk.

TABLE I.

Solid Phase $C_2H_4O_2$.

Molecular percentage of acetic acid in the liquid phase.	Temperature of equilibrium.	Molecular percentage of acetic acid in the liquid phase.	Temperature of equilibrium.
100	16·6°	85·5	− 0·3°
96·9	14·8	84·2*	− 3·0
92·4	10·8	83·4*	− 6·0
89·9	7·8	81·9*	− 9·8
88·2	4·8	80·2*	− 15·8
87·0	2·8	79·7*	− 18·2
86·2	1·0		

Solid Phase $C_6H_5{\cdot}NH_2,2C_2H_4O_2$.

85·1*	− 8·1	50·0	11·8
85·0*	− 6·1	47·5	10·4
83·25	− 0·4	45·5	9·2
82·1	2·2	44·5	8·5
81·4	5·0	42·9	7·8
80·4	7·0	41·5	6·9
78·5	10·8	39·7	5·6
75·0	14·0	38·7	4·9
72·3	15·5	37·2	4·0
69·8	16·3	33·3	0·9
67·0	16·7	29·4	− 2·6
64·5	16·5	27·7	− 4·3
60·5	15·8	25·75	− 6·4
59·0	15·3	23·3	− 9·2
57·3	15·0	22·0	− 10·7
55·5	14·3	20·65	− 12·8
52·7	13·1	17·7*	− 17·0

Solid Phase $C_6H_5{\cdot}NH_2$.

0	− 6·0	16·75	− 14·9
3·0	− 7·8	21·3*	− 16·9
4·8	− 8·8	26·0*	− 19·2
10·4	− 11·8	27·5*	− 19·8
11·9	− 12·4		

Solid Phase $2C_6H_5{\cdot}NH_2,C_2H_4O_2$.

30*	− 19·8	39·4*	− 19·8
33·3*	− 19·4	41·2*	− 20·3
36·3*	− 19·4	43·2*	− 20·9

The curves show at once the existence of two compounds of the two components. The first has the composition $C_6H_5{\cdot}NH_2,2C_2H_4O_2$; its melting point is 16·7°. The second, with melting point − 19·4°, has the composition $2C_6H_5{\cdot}NH_2,C_2H_4O_2$, and is metastable under all conditions. These, with pure aniline and acetic acid, were the only solid phases obtained. A compound corresponding with the

formula $C_6H_5{\cdot}NH_2,C_2H_4O_2$ was not found. Great supercooling was necessary to cause the compound $C_6H_5{\cdot}NH_2,2C_2H_4O_2$ to separate. This accounts for the somewhat lengthy, metastable prolongations of the curves for the other solid phases. Mixtures containing a large proportion of acetic acid became exceedingly viscous at low temperatures, such as $-35°$. The compound $C_6H_5{\cdot}NH_2,2C_2H_4O_2$, in contrast with the other solid phases, was slow to come to equilibrium with the liquid; hence the whole of the curve for this solid phase was worked out by the analytical method. The other curves were obtained in the usual manner.

The invariant points where the compound $C_6H_5{\cdot}NH_2,2C_2H_4O_2$ exists in equilibrium with the liquid phase and acetic acid and aniline are at temperatures of $-2{\cdot}4°$ and $-15{\cdot}6°$ respectively. The compound $2C_6H_5{\cdot}NH_2,C_2H_4O_2$ coexists with aniline and solution at $-19{\cdot}8°$.

It is intended to work out some binary systems of a similar nature and to compare the results with those described above.

Summary.

(1) Equilibria in the binary system, aniline–acetic acid, have been determined.

(2) There is no evidence of the existence of a compound $C_6H_5{\cdot}NH_2,C_2H_4O_2$.

(3) Two new compounds, $C_6H_5{\cdot}NH_2,2C_2H_4O_2$ and

$$2C_6H_5{\cdot}NH_2,C_2H_4O_2,$$

the latter metastable, have been shown to exist.

In conclusion, I must express my thanks to Dr. A. C. D. Rivett for suggesting this investigation, and to Professor T. H. Laby for assistance in standardising the thermometers used.

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L.—*Equilibria of Hydrofluosilicic Acid.*

By LAWSON JOHN HUDLESTON and HENRY BASSETT.

PART I.

IN some recent work involving the use of hydrofluoric acid we found that, on titration, an appreciable time was required to obtain the true end-point. Thus, when phenolphthalein was used as

indicator, an apparently considerable excess of alkali could be run in and yet the colour would fade again after a few seconds. The acid had been supplied by a thoroughly trustworthy firm as of "A. R." standard, and it left no residue on evaporation, so that its purity was not at first doubted. However, some of the work described below was carried out with it and proved that the effect observed was due to a large proportion of hydrofluosilicic acid.

We repeated the "A. R." test ourselves. This consists (List of Reagents for Analytical Purposes with Notes indicating the Standards of Purity regarded as necessary for Analytical Work) in adding an excess of a solution of potassium chloride to the solution to be tested, when a turbidity, due to potassium silicofluoride, should be observed. However, no such turbidity appeared, doubtless owing to the formation of a colloidal solution, all the less easily detected by the eye, as vessels only of wax or platinum were admissible.

Katz (*Chem. Zeit.*, 1904, **28**, 356, 387) developed a quantitative method of determining the proportions in which these two acids might occur together in mixtures. He added potassium chloride, as in the "A. R." test, but he also added alcohol to decrease the solubility of potassium silicofluoride and then titrated the solution. The hydrofluosilicic acid was removed according to the equation $H_2SiF_6 + 2KCl = K_2SiF_6 + 2HCl$, thus liberating an equivalent quantity of hydrochloric acid. He then titrated an equal volume of the solution directly, and in this case, with phenolphthalein as indicator, the reaction took a different course, represented by the equation $H_2SiF_6 + 6NaOH = 6NaF + H_2SiO_3 + 3H_2O$. Hence, if the first titration required *a* c.c. of alkali and the second *b* c.c., then $\frac{\frac{3}{2}(b-a)}{b}$ was the proportion of alkali neutralised (in the second case) by the hydrofluosilicic acid. Katz himself stated that the results were not accurate owing to the absorption of hydrofluoric acid by the colloidal precipitate, and he introduced corrective factors, which Dinwiddie (*Amer. J. Sci.*, 1916, **42**, 421) further modified. The method developed in this paper is free from these defects, though rather more lengthy. Before describing this, however, it should be mentioned that a portion of our acid was diluted until about $0{\cdot}75N$ and titrated by Katz's method. The first titration required 12·90 c.c. and the second 19·00 c.c. Thus the proportion of hydrofluosilicic acid (by equivalents) was 48 per cent., or the solution contained 52 mols. of hydrogen fluoride to 8 mols. of hydrofluosilicic acid (uncorrected).

For the complete neutralisation of hydrofluosilicic acid according

to the equation $H_2SiF_6 + 6NaOH = 6NaF + H_2SiO_3 + 3H_2O$ an appreciable time is required, as mentioned by Wagner and Ross (*J. Ind. Eng. Chem.*, 1917, **9**, 1116), but, so far as we have been able to discover, no quantitative study of it has been previously made. Yet it offers another method of studying the composition of mixtures of the two acids, as indicated below. Vessels of waxed glass, or sometimes of pure wax, were used throughout the experiments Small test-tubes containing weighed quantities of the mixed acids were placed upright in conical flasks containing measured quantities of sodium hydroxide solution coloured with a few drops of phenolphthalein. The flasks were then closed with rubber stoppers and the liquids mixed by inverting the vessel and shaking vigorously, the time from this moment until the colour (clearly visible through the wax) faded being measured by a stop-watch. The flasks were then opened and further alkali run in until the solution was permanently neutralised. It was obvious that a portion of the hydrion that the solution could ultimately furnish was produced but slowly, probably because it was "bound" in a complex. Further, if n c.c. of alkali were originally present in the flask and N c.c. were required for total, permanent neutralisation, $\frac{N-n}{N} \times 100$ was the percentage of the total hydrion in the "bound" condition at the moment when the colour faded. This term we have denoted by C in the tables that follow. Moreover, during the period timed, the solution was alkaline, so the method allows of the study of the kinetics of the reaction: "bound" hydrion→"available" hydrion, undisturbed by any opposing reactions.

The first experiment was carried out in this way at 19·2° with the mixed acid described above, after dilution to 1·8N, the alkali being 0·184N. The time of fading, t, was measured in seconds.

TABLE I.

1·8N-*Acid*; 0·184N-*Sodium Hydroxide*; *Temperature* 19·2°.

	C.	t.	C.	t.	C.	t.	C.	t.
	32·80	2·2	16·45	19·0	7·95	39·8	5·64	44·8
	31·75	2·6	16·60	19·2	8·20	39·0	3·70	59·0
	31·65	3·0	16·70	19·4	7·46	38·0	4·28	54·1
Mean	32·07	2·6	16·58	19·2	7·87	38·6	4·54	52·6

The logarithms of these values of C plotted against the times give a straight line, which is the familiar curve of a unimolecular reaction. From the four mean results six values of the velocity

constant can be calculated, and, by the help of the mean obtained, four values for the initial value of C (denoted by C_0) may then be calculated. C_0 is thus a measure of the original concentration of the "complex" present in the unneutralised acid. The values for the velocity constant (calculated for ordinary logarithms) are: 0·01694; 0·01698; 0·01668; 0·01684; 0·01707; 0·01725; mean 0·01696. Converted for natural logarithms, this becomes 0·0390. The agreement is very satisfactory. For the values of C_0 we have: 35·49; 35·10; 35·55; 35·43, the best value probably being 35·50.

In Experiment 2 these determinations were repeated with solutions brought previously to 25·0° in a thermostat. The results are given in table II, where the velocity constant and C_0 have been calculated and the deviations from the theoretical curve are shown. In the early part of the curve small errors in t cause large errors in C, whilst in the later part the reverse is the case. Hence both must be shown, and the second column gives the values of t calculated from the observed values of C, whilst the eighth column gives the values of C calculated from the observed times.

TABLE II.

1·8N-Acid; 0·184N-Sodium Hydroxide; Temperature 25·0°.
$C_0 = 39·0$; $k = 0·0748$ (*for natural logs*).

Time of fading in seconds.			C.c. of alkali added.		C.		
Obs.	Calc.	Diff.	Initial.	Total.	Found.	Calc.	Diff.
5·2	4·3	+ 0·9	*14·70*	*20·50*	28·3	26·5	+ 1·8
3·8	4·3	− 0·5	*15·30*	*21·30*	28·2	29·4	− 1·2
13·2	13·2	nil	*17·75*	*20·75*	14·5	14·5	nil
13·8	13·8	nil	*17·65*	*20·50*	13·9	13·9	nil
21·0	22·2	− 1·2	*18·80*	*20·30*	7·4	8·1	− 0·7
29·0	28·6	+ 0·4	*18·55*	*19·45*	4·6	4·5	+ 0·1
33·0	33·8	− 0·8	*20·15*	*20·80*	3·1	3·2	− 0·1
33·0	32·2	+ 0·8	*19·40*	*20·10*	3·5	3·3	+ 0·2

It is unfortunate that this acid was not again checked at the lower temperature, for, in the light of subsequent work, it appears almost certain that it had become contaminated with silica. As will be seen later, it is almost certain that with a mixture of this kind C_0 is independent of the temperature (see p. 415).

A third experiment was then made with the acid diluted nearly forty times. No high degree of precision was aimed at here, and only a few determinations were made, as we wanted to determine merely whether C_0 varied greatly with dilution or not. The results are collected in table III.

TABLE III.

0·05N-Acid; 0·184N-Sodium Hydroxide; Temperature 25·0°.
C_0 = 35·0; k = 0·0640 (*for natural logs.*).

Time of fading in seconds.			C.c. of alkali added.		C.		
Obs.	Calc.	Diff.	Initial.	Total.	Found.	Calc.	Diff.
6·4	6·5	− 0·1	*4·00*	*5·20*	23·1	23·2	− 0·1
9·2	9·5	− 0·3	*4·25*	*5·25*	19·0	10·4	− 0·4
14·0	14·0	nil	*4·50*	*5·25*	14·3	14·3	nil
19·8	20·4	− 0·6	*4·75*	*5·25*	9·5	9·8	− 0·3
31·5	30·9	+ 0·5	*5·00*	*5·25*	4·8	4·7	+ 0·1

The lower value of k obtained is satisfactorily accounted for by the smaller effect of the heat of reaction of this dilute solution, as will be shown later (see below). The theory developed in Part III of this paper, formulated many months after the measurements were made, requires that the value of C_0 should be slightly less for a very dilute solution of the mixed acid, but it is not possible to say whether this result confirms the valne obtained in experiment II or not.

Further experiments were attempted at 0°, but the cooling was unsatisfactory and the results are not worth recording. They offered further evidence, however, that the value of C_0 in experiment II was too high, that is, the particular solution used had been contaminated.

The errors involved in these experiments vary very much from case to case. For instance, control experiments showed that the bulk of the liquids was mixed by this method in a fraction of a second, but the time required for the last trace of the contents of the test-tube to be completely washed out might be two seconds. Hence time readings of this order were untrustworthy; the larger values, however, were not seriously affected. Again, the end-point was not very sharp, especially for the dilute solution. For the concentrated solutions, C should be accurate to 0·25 per cent., but for the dilute solution, where a total of only 5·25 c.c. of sodium hydroxide solution was used, C could not be determined with a greater accuracy than 1 per cent. Again, the precise instant when the colour faded was difficult to determine for low values of C, because in these cases it faded so gradually, and it was difficult to see a very faint colour through the wax.

There is also the question of the rise of temperature due to the heat of the reaction. The production of 1 gram-equiv. of sodium fluoride from hydrofluoric acid and sodium hydroxide is accompanied by the production of about 16,000 cals. Thus, neglecting the

heat changes associated with the production of hydrogen fluoride from hydrofluosilicic acid, and the fact that the solution was never completely neutralised by the alkali with which it was mixed in the first instance, and also disregarding the heat absorbed by the containing vessel or lost by radiation, the maximum possible rise of temperature would be $16/V$, where V is the volume in litres containing 1 equiv. of the sodium fluoride formed. The value of this is 2·6° for the solutions in experiments 1 and 2, and 0·8° for the solution in experiment 3.

Part II.

The Product of the Action of Silicon Tetrafluoride on Water.

What was expected to be pure hydrofluosilicic acid was prepared by passing silicon tetrafluoride into water contained in vessels of either wax or silica (it was feared that glass might give rise to the production of sodium fluoride) and filtering the product from the precipitated silica through a wax funnel into a wax vessel. The silicon tetrafluoride was prepared (1) by the action of concentrated sulphuric acid on a mixture of sand and calcium fluoride, (2) by the action of concentrated sulphuric acid on potassium silicofluoride, and (3) by heating barium silicofluoride, but there was no apparent difference in the product. In all cases the solution was left in contact with the precipitated silica for at least twenty-four hours before filtering, to ensure that the concentration of any hydrofluoric acid formed should fall to its equilibrium value.

The apparatus used for the fading experiments was slightly modified. Wax cylinders were made, having for half their length a vertical wax partition, which divided the lower portion into two water-tight cells in which the acid and the alkali could be separately placed. The cylinders were closed with rubber stoppers, and, as before, mixing was secured by inverting and shaking the vessel, but the form of the apparatus allowed much more rapid washing out of both compartments. It also permitted the use of solutions of approximately equal strength, since each cell held 20 c.c., a volume that can be measured with reasonable accuracy. For the acid, pipettes of the so-called "automatic" type were made of pure wax. These are capable of considerable accuracy; for instance, in the calibration of one, three successive deliveries weighed 9·977, 10·003, and 9·898 grams respectively. The sodium hydroxide was made by placing freshly cut sodium in a platinum dish over water in a closed vessel which was then evacuated. The violence of the reaction between the water-vapour and the sodium could be easily controlled by regulating the pressure. The solution thus obtained

was diluted with freshly boiled water and stored in an iron vessel, from which it was siphoned off through a copper tube. It appeared to be completely free from silica and carbonate.

Experiment 4 was carried out in this apparatus with a solution of hydrofluosilicic acid prepared as described and filtered from the precipitated *silicic acid*, in order to trace the rate of decay of C throughout the length of the curve. The results were considerably less regular than those obtained previously, as the thermostat was acting irregularly. Nevertheless, as table IV shows, it is clear that the curve is logarithmic. The total alkali used in this case was only 7·8 c.c., so that C should be correct to 1 per cent.

TABLE IV.

10 c.c. of 0·3N-Hydrofluosilicic Acid and 0·38N-Sodium Hydroxide. Temperature 15·3° (? 16·4°); $C_0 = 55{\cdot}5$; $k = 0{\cdot}0270$.

Time of fading.			C.c. of alkali added.		C.		
Found.	Calc.	Diff.	Initial.	Total.	Found.	Calc.	Diff.
19·4	19·8	− 0·4	*5·20*	*7·70*	32·5	32·9	− 0·4
18·6	20·4	− 1·8	*5·30*	*7·80*	32·0	33·6	− 1·6
20·0	22·9	− 2·9	*5·40*	*7·70*	29·9	32·4	− 2·5
22·0	22·4	− 0·4	*5·40*	*7·75*	30·3	30·6	− 0·3
24·0	24·0	nil	*5·50*	*7·75*	29·0	29·0	nil
4·4	3·1	+ 1·3	*3·80*	*7·75*	51·0	49·3	+ 1·7
2·8	0·9	+ 1·9	*3·60*	*7·85*	54·2	51·5	+ 2·7
3·2	1·8	+ 1·4	*3·70*	*7·85*	52·9	50·9	+ 2·0
3·0	2·7	+ 0·3	*3·80*	*7·85*	51·6	51·3	+ 0·3
5·0	3·1	+ 1·9	*3·85*	*7·85*	51·0	48·5	+ 2·5
7·0	6·6	+ 0·4	*4·20*	*7·85*	46·5	45·9	+ 0·6
4·2	4·1	+ 0·1	*3·90*	*7·75*	49·7	49·6	+ 0·1
6·4	7·9	− 1·5	*4·30*	*7·80*	44·9	46·6	− 1·7
11·0	11·8	− 0·8	*4·60*	*7·70*	40·3	41·2	− 0·9
17·0	18·0	− 1·0	*5·10*	*7·75*	34·2	35·0	− 0·8
30·0	31·2	− 1·2	*5·90*	*7·75*	23·9	24·7	− 0·8
33·4	39·7	− 6·3	*6·20*	*7·65*	19·0	22·5	− 3·5
55·4	55·5	− 0·1	*6·70*	*7·65*	12·4	12·4	nil
38·4	36·9	+ 1·5	*6·20*	*7·80*	20·5	19·7	+ 0·8
51·6	50·8	+ 0·8	*6·70*	*7·80*	14·1	13·8	+ 0·3
62·2	60·0	+ 2·2	*6·85*	*7·70*	11·0	10·4	+ 0·6
73·0	66·6	+ 6·4	*6·95*	*7·65*	9·2	7·7	+ 1·5
95·4	99·3	− 3·9	*7·50*	*7·80*	3·8	4·2	− 0·4
97·2	92·2	+ 5·0	*7·30*	*7·65*	4·6	4·0	+ 0·6
59·0	60·6	− 1·6	*7·00*	*7·85*	10·8	11·3	− 0·5
60·0	58·7	+ 1·3	*7·00*	*7·90*	11·4	11·0	+ 0·4

In experiment 5 the effect of dilution was studied with a similar preparation. Naturally the dilution was effected after filtration in each case, and, as will be seen from table V, no difference could be observed in the value of C_0. However, as will be explained later, the concentration at which the solution was filtered from the silica did make a difference in the equilibrium values, and the value of

C_0, therefore, was not the same as that in the previous experiment. Unfortunately, this was not realised at the time, and no record was kept of the temperatures and concentration at which the various preparations were filtered.

TABLE V.

The Effect of Dilution on the Initial Concentration of the Complex. Temp. 15·2°; $C_0 = 54{\cdot}7$; $k = 0{\cdot}025$ (*for natural logs.*).

18·85 c.c. of 0·32 *N*-Hydrofluosilicic acid and 0·323*N*-Sodium Hydroxide.

Time of fading.			C.c. of alkali added.		*C*.		
Found.	Calc.	Diff.	Initial.	Total.	Found.	Calc.	Diff.
6·8	6·3	+ 0·5	*10·00*	*18·75*	46·7	46·2	+ 0·5
10·0	12·1	− 2·1	*11·00*	*18·50*	40·5	42·6	− 2·1
16·6	17·3	− 0·7	*12·00*	*18·60*	35·5	36·1	− 0·6
20·4	23·4	− 3·0	*13·00*	*18·70*	30·5	32·9	− 2·4
30·4	31·2	− 0·8	*14·00*	*18·70*	25·1	25·6	− 0·5
40·2	40·2	nil	*15·00*	*18·75*	20·0	20·0	nil
50·6	53·1	− 2·5	*16·00*	*18·70*	14·5	15·4	− 0·9
80·0	73·1	+ 6·9	*17·00*	*18·65*	8·8	7·4	+ 1·4
18·85 c.c. of 0·15*N*-Hydrofluosilicic acid and 0·16*N*-Sodium hydroxide.							
0·2	9·9	+ 0·3	*10·00*	*17·45*	42·7	42·4	+ 0·3
16·0	15·8	+ 0·2	*11·00*	*17·45*	36·9	36·7	+ 0·2
28·4	29·3	− 0·9	*13·00*	*17·65*	26·3	26·9	− 0·6
38·4	39·9	− 1·5	*14·00*	*17·55*	20·2	21·0	− 0·8
53·8	52·3	+ 1·5	*15·00*	*17·60*	14·8	14·3	+ 0·5
67·0	69·6	− 2·6	*16·00*	*17·70*	9·6	10·2	− 0·6
58·0	53·1	+ 4·9	*15·00*	*17·55*	14·5	12·8	+ 1·7
18·85 c.c. of 0·078*N*-Hydrofluosilicic acid and 0·087*N*-Sodium hydroxide.							
4·8	3·4	+ 1·4	*8·50*	*17·05*	50·2	48·5	+ 1·7
9·0	8·6	+ 0·4	*9·50*	*17·00*	44·1	43·7	+ 0·4
12·4	15·3	− 2·9	*10·50*	*16·75*	37·3	40·1	− 2·8
22·0	21·3	+ 0·7	*11·50*	*16·95*	32·1	31·6	+ 0·5
26·4	28·7	− 2·3	*12·50*	*17·95*	26·7	28·3	− 1·6
45·0	41·9	+ 3·1	*13·50*	*16·70*	19·2	17·8	+ 1·4
56·6	57·8	− 1·2	*14·50*	*16·65*	12·9	13·3	− 0·4
77·4	76·9	+ 0·5	*15·55*	*16·90*	8·0	7·9	+ 0·1

In experiment 6 the effect of temperature on both the velocity constant and the value of C_0 was studied. The solution was not affected by keeping or by contamination, because some of the readings at 15° were made at the beginning of the whole experiment and the remainder at the very end, yet they lay on the same curve. The results are collected in table VI.

The usual formula for the variation of a velocity constant with temperature is $\log k = -\frac{A}{T} + C$, where T is the absolute temperature and A and C are constants. Table VI records the values of k

TABLE VI.

The Effect of Temperature on the Initial Concentration of the Complex and on the Velocity Constant.

10·0 c.c. of 0·18*N*-Hydrofluosilicic Acid and 0·12*N*-Sodium Hydroxide.

Time of fading.			C.c. of alkali added.		*C*.		
Found.	Calc.	Diff.	Initial.	Total.	Found.	Calc.	Diff.
Temp. 15·0°. C_0 = 53·0.			k = 0·024 (for natural logs).				
19·0	18·9	+ 0·1	*10·20*	*15·40*	33·7	33·6	+ 0·1
14·0	13·7	+ 0·3	*9·50*	*15·50*	38·7	37·9	+ 0·8
9·4	8·9	+ 0·5	*8·80*	*15·40*	42·8	42·3	+ 0·5
3·0	3·1	− 0·1	*8·00*	*15·75*	49·2	49·3	− 0·1
3·6	3·8	− 0·2	*8·00*	*15·50*	48·4	48·6	− 0·2
4·4	1·6	+ 2·8	*7·80*	*15·90*	50·9	47·7	+ 3·2
2·6	1·1	+ 1·5	*7·60*	*15·70*	51·6	49·8	+ 1·6
2·0	4·0	− 2·0	*8·20*	*15·80*	48·1	50·5	− 2·4
2·8	5·2	− 2·2	*8·40*	*15·80*	46·8	49·6	− 2·8
6·4	6·4	nil	*8·60*	*15·80*	45·5	45·5	nil
6·0	7·5	− 1·5	*8·80*	*15·80*	44·3	45·9	− 1·6
2·0	1·4	+ 0·6	*8·00*	*16·40*	51·2	50·5	+ 0·7
6·8	6·4	+ 0·4	*9·00*	*16·50*	45·4	45·0	+ 0·4
12·4	12·6	− 0·2	*10·00*	*16·45*	39·2	39·4	− 0·2
19·0	19·9	− 0·9	*11·00*	*16·40*	32·9	33·6	− 0·7
27·6	28·4	− 0·8	*12·00*	*16·40*	26·8	27·3	− 0·5
Temp. 25·0°. C_0 = 57·0.			k = 0·075 (for natural logs).				
2·0	1·7	+ 0·3	*8·00*	*16·00*	50·0	49·1	+ 0·9
8·4	8·1	+ 0·3	*11·00*	*16·00*	31·2	30·3	+ 0·9
6·4	5·6	+ 0·8	*10·00*	*16·00*	37·5	35·2	+ 2·3
2·2	2·7	− 0·5	*8·50*	*15·85*	46·4	48·3	− 1·9
4·4	3·8	+ 0·4	*9·00*	*15·75*	42·8	41·0	+ 1·8
4·2	4·7	− 0·5	*9·50*	*15·85*	40·0	41·6	− 1·6
5·6	5·9	− 0·3	*10·00*	*15·80*	36·7	37·4	− 0·7
9·6	10·4	− 0·8	*10·50*	*14·30*	25·6	27·7	− 2·1
8·6	8·2	+ 0·4	*11·00*	*15·90*	30·8	29·9	+ 0·9
Temp. 0°. C_0 = 38·6.			k = 0·00385 (for natural logs).				
390	393	− 3	*15·00*	*16·40*	8·5	8·6	− 0·1
720	721	− 1	*16·00*	*16·40*	2·4	2·4	nil
300	303	− 3	*14·00*	*15·90*	12·0	12·2	− 0·2
168	168	nil	*13·00*	*16·40*	20·7	20·2	+ 0·5

determined at three temperatures, and hence, by taking the equations in pairs, three values of the constant C may be obtained, namely: 29·5, 29·8 and 30·2 (mean 29·83). Thence three values of A may be determined, which in this case are 9661, 9665, and 9661 (mean 9662).

Hence, for this reaction, $\log k = -\frac{9662}{T} + 29{\cdot}83$. In table VII, T, calculated by inserting in this equation the velocity constants obtained, is compared with the values recorded in the previous experiments.

TABLE VII.

Experiment	k	T obs.	T calc.	Diff.
1	0·0390	292·2	292·2	nil
2	0·0748	298·0	298·1	− 0·1
3	0·0640	298·0	296·6	+ 1·4
4	0·0270	288·3 (?)	289·0	− 0·7
5	0·0250	288·2	288·4	− 0·2
6 (a)	0·0240	288·0	288·0	nil
6 (b)	0·0750	298·0	298·1	− 0·1
6 (c)	0·00385	273·0	273·0	nil

This neglects the influence of the heat of reaction, which is a somewhat indefinite factor. Thus the maximum possible difference in temperature in experiments 2 and 3 from this cause is 1·8° (see p. 408), whilst in the above table it appears that the actual difference, as calculated from the velocity constants, in these two cases is 1·5°.

PART III.

Theoretical Discussion.

When silicon tetrafluoride is passed into water the reaction may be expressed by the equations:

(1) $SiF_4 + 3H_2O = H_2SiO_3 + 4HF.$

(2) $SiF_4 + 2HF = H_2SiF_6$

and (3) $3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3$, by addition.

The reactions must be reversible, since hydrofluosilicic acid is formed equally by the action of silicon tetrafluoride on water and of hydrofluoric acid on silica, and also hydrofluosilicic acid with sufficient alkali yields, ultimately, sodium fluoride and silicic acid. Therefore all four substances must be present in finite, even though possibly very small, concentration in these solutions. Further, *these solutions, filtered from the precipitated silicic acid, on titration* by Katz's method, react like pure hydrofluosilicic acid, so that the free hydrofluoric acid cannot be in excess of that required to combine with the free silicon tetrafluoride and silicic acid to form hydrofluosilicic acid. Katz's method, however, cannot detect free silicon tetrafluoride, since by the precipitation of potassium silicofluoride the equilibrium of equation (3) would be shifted completely to the right in any case.

Consider a volume, V, of a solution prepared by passing silicon tetrafluoride into water and filtering off the precipitated silicic acid. Let there be a mols. of hydrofluosilicic acid, b mols. of silicon tetrafluoride, x mols. of hydrogen fluoride, and y mols. of silicic acid present. Ultimately the solution will yield $6a + 4b + x$ equivs. of hydrion, but a fraction of this, $\frac{C_a}{100}$, will be in a form

from which it will be liberated only slowly, by a unimolecular reaction in alkaline solution. So far as the nature of this reaction is concerned, it might be the hydrolysis of silicon tetrafluoride [equation (1)], but the velocity with which this compound reacts with water in the preparation, and, still more, considerations of the equilibria involved, indicate that the slow reaction studied is not this, but the dissociation of sodium silicofluoride according to the equation $Na_2SiF_6 \rightleftharpoons 2NaF + SiF_4$, whilst the hydrolysis of silicon tetrafluoride, the neutralisation of hydrofluoric acid, and the neutralisation of hydrofluosilicic acid to produce sodium silicofluoride proceed with immeasurable rapidity. Hence, on mixing the solution with alkali,

hydrofluosilicic acid neutralises $2a$ equivs. rapidly and a further $4a$ equivs. slowly.
silicon tetrafluoride neutralises $4b$ equivs. rapidly,
hydrofluoric acid neutralises x equivs. rapidly,

and silicic acid is without action on the indicator.

The silicic acid might be present in colloidal solution, so we have no authority as yet to assume that its "active mass" is proportional to its concentration. We will therefore denote the "active mass" in this case by the formula in open brackets. The equilibrium relations corresponding with equations (1), (2), and (3) are then:

$$(1a)\ [SiF_4] = K_1 \times [HF]^4 \times (H_2SiO_3).$$
$$(2a)\ [SiF_4] \times [HF]^2 = K_2 \times [H_2SiF_6].$$
$$(3a)\ [SiF_4]^3 = K_3 \times [H_2SiF_6]^2 \times (H_2SiO_3).$$

Hence in the case taken we have:

$$(1b)\ \frac{b}{V} = K_1\left[\frac{x}{V}\right]^4 (H_2SiO_3).$$
$$(2b)\ \frac{b}{a} = K_2\left[\frac{V}{x}\right]^2$$
$$(3b)\ \frac{b^3}{a^2} = VK_3\ (H_2SiO_3).$$

whilst

$$(4)\ \frac{4a}{6a+4b+x} = \frac{C_0}{100}$$

and

$$(5)\ 6a + 4b + x = K_4.$$

Experiment 5 showed that V could vary fourfold without causing appreciable variation in C_0. Hence, from equations (4) and (5), it is clear that a also is, to this extent, independent of dilution. Then, to satisfy equations (1) and (2) simultaneously, whilst at the same time having regard to the relation between the change of b and

that of x as determined by the chemical reaction, it is necessary that x should be so small that $\frac{x}{V}$ is kept constant, in spite of fourfold dilution, by the transformation of a negligible quantity of one of the other substances, so that a and b both remain sensibly constant. Then equation (3b) requires that (H_2SiO_3) shall be proportional to the concentration, that is, the "active mass" of the silicic acid can be represented in the usual way as $\frac{y}{V}$. We think it probable that the silicic acid left after filtration is in true solntion.

Hence, for solutions prepared by passing silicon tetrafluoride into water and filtering off the precipitated silicic acid, we are led to believe that, on dilntion, the relative quantities of hydrofluosilicic acid, silicon tetrafluoride, and silicic acid remain sensibly unaltered whilst the concentration of free hydrofluoric acid, which must be extremely small, is maintained constant by the hydrolysis of negligible quantities of the first two substances. This is in harmony with the fact that sodium silicofluoride is so slightly dissociated, in the sense of equations (1) and (2), that the concentration of hydrion to which it gives rise is not enough to affect methyl-orange, and also with the fact that if solutions of the kind under discussion are neutralised with sufficient alkali to show the fading effect, whilst still being not completely neutralised, they show the effect again with a single drop of alkali, that is, they give rise to very little silicon tetrafluoride. It should be remembered in this connexion, however, that it is not necessary that the equilibrium constant of the sodium salt should be the same as that of the corresponding acid. While the solution is in contact with precipitated silicic acid, it must be supposed that the concentration of the latter in true solution is constant; hence equation (3b) will not, in this case, be independent of the concentration. This accounts for the different values of C_0, obtained at the same temperature, in experiments 4, 5, and 6, which were made with different preparations filtered at different concentrations. At 15° the value of C_0 varied between 53 and 55·5. If $C_0 = 54{\cdot}54$ (which is a convenient number for calculation), $a = 13{\cdot}64$ (equation 4) and $b = 4{\cdot}55$, since x is negligible and $6a + 4b + x = 100$ (C_0 being a percentage). Hence $\frac{b}{a} = \frac{1}{3}$. From equation (2$b$)$K_2 = \frac{b}{a}\left[\frac{x}{V}\right]^2$. The last term being the square of a small quantity is itself a very small quantity, so that $K_2 = \frac{1}{3}$ of a very small quantity and is itself very small. It is possible to form some estimate of its value from experiments 2 and 3. These experiments were made with the mixed acids

containing a considerable proportion of free hydrofluoric acid. Hence from equation (2*b*), since K_2 is small and x is here large, the concentration of silicon tetrafluoride must be very small, and great differences in its *ratio* can be brought about by transformations of negligible quantities of the other substances. Equation (2*b*) may be rewritten in the form $b = K_2V^2a/x^2$, from which it is clear that as a and x do not change appreciably, b is proportional to V^2. If the volumes containing 100 equivs. are considered, in experiment 2, $C_0 = 39·0$ and in experiment 3, $C_0 = 35·0$. Therefore at most the silicon tetrafluoride has increased by 4 equivs. or 1 mol. for a forty-fold dilution. Hence $b + 1 = 1600\ b$, or b is negligible. The dilute solution used in experiment 3 was $0·05N$, therefore the volume containing 100 equivs. was 2000 litres. Hence the composition of this solution is approximately:

$$SiF_4 = 0·0005 \text{ mol. per litre.}$$
$$H_2SiF_6 = 0·0045 \text{ mol. per litre.}$$
$$HF = 0·021 \text{ mol. per litre.}$$

therefore $$K_2 = \frac{0·0005 \times 0·0004}{0·0045} \approx 4 \times 10^{-5}.$$

The data were not sufficiently accurate for this to be accepted as a final value, but it indicates the order.

It will be seen that for the stronger solutions the concentration of silicon tetrafluoride is very small, so that it should not be possible for C_0, which is proportional to the concentration of hydrofluosilicic acid, to increase perceptibly on changing the temperature. This leads us to suppose that the solution used in experiment 2 had actually a greater silicon content than that used in experiment 1, and there is also practical reason to believe that contamination occurred.

Finally, some idea of the possible concentration of the silicic acid in solution can be obtained from a consideration of experiment 6. At 15° the value of C_0 was 53·0, hence the volume containing 100 equivs. had 13·25 mols. of hydrofluosilicic acid, whilst at 0° the value of C_0 had fallen to 38·6, so the same volume contained 9·65 mols. of hydrofluosilicic acid. Hence 3·6 mols. of the acid had been converted into silicon tetrafluoride, and therefore at the same time 7·2 mols. of hydrofluoric acid must have been produced. As K_2 is very small and there is a considerable proportion of silicon tetrafluoride, all this acid must have been converted into silicon tetrafluoride by the silicic acid present, that is, at least 1·8 mols. of silicic acid must have been present in this volume at 15°. The solution was $0·18N$, and therefore the volume containing 100 equivs. was 550 litres; hence the silicic acid must

have been present to an extent of at least 0·003 mol. per litre, apparently in true solution, since its "active mass" varied with dilution in the ordinary way.

Summary.

(1) The existing "A. R." method of testing for silica in hydrofluoric acid is shown to be inadequate.

(2) A method of measuring the proportion of hydrofluosilicic acid in mixtures of this with hydrofluoric acid is described.

(3) The rate of dissociation of sodium silicofluoride into silicon tetrafluoride and sodium fluoride has been determined, together with the formula for the variation of the velocity constant with temperature.

(4) It is shown that silicic acid can exist in solution, with an active mass proportional to its concentration, to the extent of at least 0·003 mol. per litre at 15°.

(5) The equilibria set up when silicon tetrafluoride is passed into water are discussed, and it is shown that the resulting solution contains a considerable proportion of unchanged silicon tetrafluoride.

In conclusion, we should like to make acknowledgment to the Salters' Institute of Industrial Chemistry for providing the Fellowship which made the research possible.

UNIVERSITY COLLEGE,
READING. [*Received, January 7th,* 1921.]

LI.—*The System, Picric Acid–5-Phenylacridine.*

By HENRY BASSETT and THOMAS ARTHUR SIMMONS.

IN preparation for some work which was contemplated, it became necessary to examine the fusion diagram of the system, picric acid–phenylacridine. Results worth recording have been obtained. The substances used were purified by crystallisation, and the method employed was the usual one of determining the temperatures at which various mixtures of known composition began to solidify. The mixture was melted in a tube immersed in a bath of paraffin wax. The tube was fitted with a cork with two holes, through which passed a glass stirrer and a thermometer with its bulb completely immersed in the molten liquid.

The bath was allowed to cool so that the temperature of the mixture fell about 1° per minute, the mixture being stirred gently and its temperature read every half-minute until it was just below

the freezing point as found from a first determination. The mixture was then stirred more vigorously until crystallisation began and the temperature rose to the freezing point and remained constant for one and a half to two minutes.

The freezing points of the various mixtures are shown in the table. The temperatures have been corrected for the error of the thermometer and also for the error due to the exposed part of the stem.

The known picrate of phenylacridine (one molecule of picric acid to one molecule of phenylacridine) is clearly indicated with a stable melting point, 227·7°. There is also definite indication of a second compound (two molecules of picric acid to one molecule of phenylacridine) with an unstable melting point at about 180°.

Attempts to isolate the latter compound by mixing hot or cold alcoholic or benzene solutions in correct proportion or with a slight excess of picric acid always resulted in the separation of the compound melting at 227·7°, but on mixing cold, concentrated, alcoholic solutions in the proportion of five molecules of picric acid to one molecule of phenylacridine a precipitate was obtained which, after being filtered, washed once with alcohol, and dried, softened at 178° and melted at 185—186°. This was the new *compound of two molecules of picric acid with one molecule of* phenylacridine. (Found: N = 13·3. $C_{31}H_{19}O_{14}N_7$ requires N = 13·74 per cent.)

In appearance the two picrates are very similar, although the compound containing two molecules of picric acid is somewhat yellower than the other.

Molecular percentages of phenyl-acridine.	Freezing point.	Molecular percentages of phenyl-acridine.	Freezing point.	Molecular percentages of phenyl-acridine.	Freezing point.
0·00	120·3°	29·25	175·6°	58·42	215·7°
1·00	119·8	30·00	176·2	65·54	201·1
1·88	119·3	30·66	178·2	76·10	175·1
3·07	118·8	31·00	180·4	76·94	172·0
4·02	122·3	31·20	181·4	78·00	169·4
7·31	132·4	35·00	195·4	79·50	169·9
12·53	145·4	43·15	217·2	82·03	170·7
20·72	161·7	48·75	226·4	87·06	172·5
24·91	168·8	50·00*	227·7	95·40	178·2
26·40	171·2	50·75	226·4	100·00	181·9
28·00	173·6	52·10	225·1		

* The same freezing point was obtained for the 50 (molecular) per cent. mixture prepared by weighing out the dry constituents as for the phenylacridine picrate previously prepared and crystallised from alcohol.

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READING. [*Received, February 1st, 1921.*]

LII.—*ββ'-Dichlorodiethyl Disulphide.*

By GEORGE MACDONALD BENNETT.

THE action of ethylene upon the chlorides of sulphur was first observed by Despretz (*Ann. Chim. Phys.*, 1822, [ii], **21**, 428), who obtained an unpleasant, viscous liquid. Niemann (*Annalen*, 1860, **113**, 288) obtained a small quantity of an oil, isolated by distillation in steam, which appears from its analysis to have been an impure dichlorodiethyl disulphide. About the same time, Guthrie examined the action in greater detail (*Quart. Journ. Chem. Soc.*, 1860, **12**, 116; 1861, **13**, 134; *Annalen*, 1861, **119**, 91; 1862, **121**, 110) and described a product (which had been isolated without distillation) having a density 1·346 and empirical composition, $C_4H_8Cl_2S_2$, to which the formula $CH_2Cl{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}CH_2Cl$ has been attributed in the literature. The oxidation of this product by means of nitric acid was shown by Spring and Lecrenier (*Bull. Soc. chim.*, 1887, [ii], **48**, 629) to yield the sulphonic acid, $CH_2Cl{\cdot}CH_2{\cdot}SO_3H$, which would appear to justify this point of view. Yet no experimental details were given and the evidence would not be satisfactory unless this oxidation were almost quantitative.

As the action of ethylene on sulphur monochloride at 50—70° has recently been shown to produce the monosulphide and sulphur almost quantitatively (Gibson and Pope, T., 1920, **117**, 271), whilst Green (*J. Soc. Chem. Ind.*, 1919, **41**, 469R) has obtained the monosulphide as the main product of the reaction at 100°, it seems probable that the liquid prepared by Guthrie contained a large proportion of the monosulphide.

On the other hand, the fact that the extra atomic proportion of sulphur produced in accordance with the equation

$$2C_2H_4 + S_2Cl_2 = S + S(C_2H_4Cl)_2$$

does not separate from solution when the operation is carried out at 30—40° has led Green (*loc. cit.*) to regard the product as a single substance having the formula $C_4H_8Cl_2S_2$, and since it yields the monosulphide and sulphur on distillation in a vacuum he formulates it as a disulphide of a new type, $(C_2H_4Cl)_2S{:}S$. Pope (*J. Soc. Chem. Ind.*, 1919, **38**, 432R) referred to this liquid as "some sort of pseudo-solution" of sulphur in the monosulphide, and he considered the question of its nature to be established by the fact that the sulphur was precipitated by the addition of ether or alcohol. Green, on the other hand, has usually not observed any such precipitation.

Guthrie considered that the homogeneity of his preparation was proved by the virtual identity of composition which he observed in the two portions into which the oil was separated by partial solution in 85 per cent. alcohol. The whole had previously been twice dissolved in the minimum quantity of ether. A more detailed examination has now been made of the liquid produced from ethylene and sulphur monochloride at temperatures below 35°. Its properties vary with the speed and other conditions of its preparation, but it is usually completely miscible with a small volume of ether, whilst on larger dilution with the same solvent it deposits a sulphur-yellow oil consisting mainly of sulphur, insufficient in amount, however, to account for the whole of the extra atomic proportion present in the original liquid.

These facts and the conflicting evidence mentioned above as to the precipitation of the sulphur by solvents seem to be adequately accounted for by the assumption that the liquids in question are two-phase systems in which the continuous phase is nearly pure dichlorodiethyl monosulphide and the disperse phase a liquid consisting chiefly of sulphur. The varying behaviour on dilution may be due to different degrees of dispersion, some specimens being coarse-grained emulsions, whilst others, such as the liquids obtained by Guthrie and Green, may be fine-grained or colloidal. The fact that dilution with ether does not precipitate the sulphur is not inconsistent with this view. The ether may be miscible with the continuous phase only, and the disperse phase remain practically unaffected—as is the case when cellulose nitrate sols are diluted with ether-alcohol.

In view of the observation of Spring and Lecrenier the liquid described by Guthrie requires further investigation. The steam distilled oil of Niemann and a small quantity of the reaction product isolated by Conant, Hartshorn, and Richardson (*J. Amer. Chem. Soc.*, 1920, **42**, 585) suggest that the true disulphide may be present, although the chloroethanesulphonic acid resulting on oxidation might possibly have arisen from the monosulphide, which yields this acid on oxidation with nitric acid at 100°.

The true disulphide, $CH_2Cl{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}CH_2Cl$, has now been prepared by a synthetic method through dihydroxydiethyl disulphide, $HO{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, which was obtained either by oxidation of monothioethylene glycol or by the action of sodium disulphide on ethylene chlorohydrin. The pure disulphide is a liquid closely resembling the monosulphide in many of its properties. The chlorine in it shows the ease of reaction which is so marked in the monosulphide. It is oxidised quantitatively by dilute nitric acid to chloroethanesulphonic acid.

EXPERIMENTAL.

Oxidation of ββ'-Dichlorodiethyl Sulphoxide to a Sulphonic Acid.

Three grams of the sulphoxide and 2 c.c. of fuming nitric acid were heated together in a sealed tube at 100° for ten hours. The product was diluted with water, some oil removed by extraction with ether and the solution evaporated, again diluted, and again evaporated on the water-bath. The solution was then neutralised with lead carbonate, the lead salt treated with sodium carbonate, and the aqueous solution of the sodium salt evaporated to dryness. The white residue crystallised well when its aqueous solution was evaporated in a vacuum. It consisted of sodium chloroethanesulphonate, $C_2H_4O_3ClSNa,H_2O$ (Found: $H_2O = 9{\cdot}5$; $Na = 12{\cdot}7$. Calc.: $H_2O = 9{\cdot}75$; $Na = 12{\cdot}47$ per cent.) (see *Annalen*, 1884, **223**, 213). It follows that this sulphonic acid may be produced from the dichlorodiethyl monosulphide itself.

Product of the Action of Ethylene on Sulphur Monochloride at 30—35°.

Sulphur chloride (redistilled, b. p. 136—137°) was stirred as vigorously as possible while a current of dry ethylene was passed through at such a rate that a slight excess emerged continuously. From 50 c.c. (83 grams) of the chloride were obtained 111 grams of a pale amber-coloured liquid, which deposited a trace of solid sulphur after a few hours, but thereafter remained clear.

This liquid had D^{15} 1·373. It crystallised when cooled to 0°, and then melted at 5—6°. The viscosity of this and other specimens was determined in a viscometer of the Ostwald type, water being used as a standard. For this liquid the relative viscosity at 15°, $\eta/\eta_{H_2O} = 10{\cdot}25$. (For pure dichlorodiethyl sulphide, $D^{15} = 1{\cdot}285$ and relative viscosity $(\eta/\eta_{H_2O})_{15} = 4{\cdot}85$, whence $\eta_{15} = 0{\cdot}0553$ C.G.S. units.) This relatively high viscosity is a most characteristic property of liquid–liquid two-phase systems (see, for example, Garrett, *Diss.*, Heidelberg, 1903; Hardy, *J. Physiol.*, 1905, **33**, 281). The values of the viscosity varied slightly from sample to sample, but no indication was obtained of variation with one specimen under varied mechanical treatment.

The molecular weight found by the cryoscopic method in benzene was 185. This agrees equally well with the value 191 required for a true disulphide and 175 required by a mixture of the monosulphide and sulphur in a state of aggregation represented by S_8.

Forty c.c. of the liquid, by distillation in a vacuum, gave a main fraction (35 grams), b. p. 110—120°/20 mm., m. p. 12°, and

a small quantity, b. p. 160—180°/20 mm., which probably contained polysulphides.

In another preparation 100 c.c. of sulphur monochloride were saturated with ethylene dried with greater care by means of calcium chloride. The experiment was rather protracted. Although the temperature was never higher than 35°, a cake of sulphur of the consistence of stiff butter had separated by the end of the operation. The liquid product (167 grams; D^{15} 1·295) distilled at 103—104°/12 mm. Products of higher b. p. were here almost entirely absent.

That the slowness of the reaction in the experiment just described was the cause of the separation of the sulphur seems probable from the result of a further experiment in which ethylene, similarly dried, and 50 c.c. of sulphur monochloride, to which had been added 5 c.c. of pure dichlorodiethyl sulphide to hasten the reaction, were used. In this case sulphur did not separate, and 90 c.c. of a clear liquid, D^{15} 1·316, m. p. 8·5°, were obtained. The low density compared with that of the first specimen described above is due to the absence of the small quantity of liquid of higher boiling point.

Separation of the Sulphur from the Colloidal Emulsion.

Thirty c.c. of the liquid, D 1·373, m. p. 5—6°, obtained by the reaction at 30° were diluted with dry ether. The addition of 20 c.c. of ether produced no separation into two phases. On diluting with a further 100 c.c. and shaking vigorously, a sulphur-yellow oil separated, which weighed 4·7 grams (Theory for one atomic proportion of excess sulphur = 6·7 grams). This oil was readily soluble in carbon disulphide, from which it separated unchanged on evaporation. It was left in the air at the ordinary temperature for two weeks without any sign of crystallisation, even after seeding with sulphur. It was then dried at 100° and crystallised shortly after cooling. It contained organic matter besides sulphur, and left a slight carbonaceous residue on ignition (Found: S = 80·2 per cent.).

The ethereal solution on evaporation left a liquid D^{15} 1·325, $(\eta/\eta_{H_2O})_{15}$ 6·61, m. p. 5—6°.

Another specimen of the same original preparation was heated at 100° in a current of dry air for an hour. On cooling a quantity of sulphur crystallised out, leaving a liquid, D^{15} 1·337, $(\eta/\eta_{H_2O})_{15}$ 7·24, m. p. 5—6°. The fact that the melting point was thus unaffected by the removal of sulphur shows that this had taken place without alteration in the composition of the continuous phase containing the monosulphide.

Fifty c.c. of a product, D^{15} 1·316, m. p. 8·5°, which had retained the whole of its sulphur, were frozen, and the crystals filtered with the aid of the pump. Two portions were thus separated:

(1) Twenty c.c. (from the crystals), D^{15} 1·296, $(\eta/\eta_{H_2O})_{15}$ 6·58.

(2) Thirty c.c. (from the mother liquor), D^{15} 1·336, $(\eta/\eta_{H_2O})_{15}$ 10·42.

This viscous, sulphur-yellow liquid (2) was analysed (Found: S = 41·7. $C_4H_8Cl_2S_2$ requires S = 33·5 per cent.). There was therefore present more than one atomic proportion of sulphur in excess. When this liquid was treated with an alcoholic solution of cuprous chloride as described by Hollely (T., 1920, **117**, 899), it gave the usual double salt of the monosulphide, the sulphur separating as a soft mass during the dilution with the solution of sodium chloride.

Whilst it seems clear that the sulphur is present in these liquids in a colloidal or at least a dispersed liquid condition, it is difficult to discover what special circumstances determine the formation of such systems. The separation of the sulphur after the liquid has been heated in a vacuum or in a current of air suggests that hydrogen chloride, which is always present in small quantity, may contribute to its stability. On the other hand, the cases where chlorination with evolution of hydrogen chloride has been specially noticeable during the preparation are often those where the main reaction has been slowest and the sulphur most ready to separate. All attempts to produce any such emulsion directly have hitherto failed. The introduction of plastic sulphur into the hot monosulphide, or the evaporation at a low temperature of carbon disulphide containing in solution sulphur and the monosulphide in presence or absence of a small quantity of hydrogen chloride, or of the less volatile fraction of the reaction product, were all unsuccessful. The stability of the emulsion may be influenced by the presence of a small quantity of some substance not yet considered; or the sulphur may be in a state which only arises when it is liberated from combination in an organic medium.

Preparation of Monothioethylene Glycol, $SH\cdot CH_2\cdot CH_2\cdot OH$.

The experiment described by Carius (*Annalen*, 1862, **124**, 257) has been repeated with a solution of potassium hydroxide (112 grams) in water (100 grams) saturated with hydrogen sulphide, 200 c.c. of alcohol (96 per cent.) and 80 grams of ethylene chlorohydrin, the temperature being maintained at 0°. The ultimate products were 24 grams of monothioethylene glycol and 16 grams of a viscous oil consisting of a mixture of thiodiglycol and dihydroxydiethyl disulphide with some diethylene disulphide, which

set to a waxy mass on cooling. Water or acetone separated the white disulphide, which, in this impure condition, melted at 95—100°. This substance is produced from the mercaptan by the action of the slight excess of hydrochloric acid in the solution, for it has been found that it is slowly produced when a solution of the mercaptan in dilute hydrochloric acid is allowed to stand in the cold:

$$2SH\cdot CH_2\cdot CH_2\cdot OH = C_4H_8S_2 + 2H_2O.$$

This waxy residue is no doubt similar to the substance obtained by Carius on heating his specimen on the water-bath, when the mercaptan would have been partly volatilised and partly oxidised. This may also explain the discrepancy observed by Victor Meyer (*Ber.*, 1886, **19**, 3260) between the properties of thiodiglycol as he obtained it, and those described by Carius.

The preparation of monothioethylene glycol is best conducted *in concentrated aqueous solution*: 225 grams of crystallised sodium sulphide are melted on the water-bath and saturated with hydrogen sulphide (compare Bloxam, T., 1900, **67**, 761). The solution is cooled to 50° and 70 grams of ethylene chlorohydrin are gradually added with stirring, the temperature being kept at 55—65°. The mixture is maintained at 60° for twenty minutes after the reaction has apparently subsided and then cooled, 60 c.c. of glacial acetic acid are cautiously added, and the solution, together with the sodium chloride which has separated, is extracted repeatedly with ether. The extract is dried over anhydrous sodium sulphate, and evaporated, and the residue distilled in a vacuum in a current of coal gas. The yield of the monothio-glycol is 50—55 per cent. of the theoretical.

Monothioethylene glycol is a colourless liquid, b. p. 58°/18 mm., D_4^{20} 1·1153, n_D^{20} 1·4443. It has a characteristic odour and is miscible with water.

A more detailed study of the reactions of this substance is being undertaken.

ββ'-Dichlorodiethyl Disulphide.

Monothioethylene glycol was oxidised to the corresponding dihydroxy-disulphide in aqueous solution by hydrogen peroxide, ferric chloride, or sodium hypobromite. The crude product was removed by ether and obtained as a viscous syrup. This was heated on the water-bath for an hour with four to five times its weight of concentrated hydrochloric acid, and the crude dichlorodiethyl disulphide, which separated as a yellow oil in quantity from a half to three-quarters of the weight of the monothio-glycol used, was purified by repeated fractionation in a vacuum.

An alternative method was the following. Sulphur (32 grams) was dissolved in a solution of 240 grams of hydrated sodium sulphide in 150 c.c. of water by warming, 160 grams of ethylene chlorohydrin were gradually added with shaking and cooling, and when the reaction was completed the product was removed in ether. The syrup (159 grams) obtained after evaporation of the ether, consisting of a mixture of dihydroxydiethyl disulphide with some monosulphide and higher polysulphides, was heated for an hour on the water-bath with 600 c.c. of concentrated hydrochloric acid, when 140 grams of a yellow oil separated. This oil was dried and distilled in a vacuum and yielded 70 grams of approximately pure dichlorodiethyl disulphide. The specimen contained, however, some diethylene disulphide, formed at the end of the distillation by the decomposition of some polysulphides, from which it was separated completely by fractional distillation only with great difficulty.

ββ'-Dichlorodiethyl disulphide was finally obtained as a faintly straw-coloured oil, b. p. 155°/30 mm., D_4^{20} 1·3375, $(\eta/\eta_{H_2O})_{20}$ 6·08 (Found: S = 33·67; Cl = 36·0, 35·4. $C_4H_8Cl_2S_2$ requires S = 33·50; Cl = 37·17 per cent.). A similarly low value for chlorine was obtained on analysing repeatedly distilled specimens of the monosulphide (Found: Cl = 41·8), whereas the monosulphide purified by repeated freezing gave Cl = 44·7 ($C_4H_8Cl_2S$ requires Cl = 44·6 per cent.). Purification of the disulphide by similar methods was impossible, as it could not be induced to crystallise at − 10°.

This compound resembles the monosulphide in many of its properties. It has, when pure, but little odour, but when exposed to the air for some time it develops the same characteristic "mustard" smell, which has given rise to the popular name of the monosulphide. Its vesicant action was found by comparison to be less than one-third of that of the monosulphide.

It yields a white precipitate of variable composition with an alcoholic solution of mercuric chloride. A double compound with cuprous chloride could not be obtained (compare Hollely, *loc. cit.*).

The chlorine present in the disulphide is remarkably reactive, a specimen warmed for five minutes with an alcoholic solution of potassium hydroxide yielding all its chlorine in the ionic condition. The action of aniline at 100° removes the chlorine with the production of an oil from which no crystalline derivative can be isolated. Alcoholic ammonia at 60° also removes the chlorine, but diaminodiethyl disulphide (Gabriel and Colman, *Ber.*, 1912, **45**, 1644) cannot be detected among the products. It is probable that the by-products formed in the reaction with sodium phenoxide (below) here arose in even greater proportion.

Action of Sodium Phenoxide on the Disulphide.

When dichlorodiethyl disulphide was boiled in alcoholic solution with a slight excess of sodium phenoxide (compare Helfrich and Reid, *J. Amer. Chem. Soc.*, 1920, **42**, 1208) the reaction was completed in half an hour, and when the solution was poured into a dilute aqueous solution of an alkali the oil which separated soon solidified. It was freed from impurities of unpleasant odour by repeated crystallisation from methyl alcohol and from light petroleum, and *ββ′-diphenoxydiethyl disulphide* was obtained in small, silvery plates, m. p. 96—97° (corr.) (Found : S = 21·0. $C_{16}H_{18}O_2S_2$ requires S = 20·9 per cent.).

Reaction with Sodium Sulphide.

When the dichloro-disulphide was warmed with an aqueous-alcoholic solution of sodium sulphide, a white solid was produced which melted at 100—125° and consisted of diethylene disulphide and its polymeride. The product on heating gave a sublimate, m. p. 110°, which was not depressed by admixture of diethylene disulphide.

Oxidation of ββ′-Dichlorodiethyl Disulphide.

The dichloro-disulphide was oxidised by hydrogen peroxide (2 atom. O) in glacial acetic acid solution, a yellow liquid being obtained, which could not be induced to crystallise.

ββ′-Dichlorodiethyl disulphide (1 gram) was warmed with dilute nitric acid until it dissolved, the solution was evaporated twice on the water-bath, and the residue dissolved in water. The solution was boiled with lead carbonate, the lead salt obtained (2·4 grams) was dried at 100°, and converted into the ammonium salt by boiling with a solution of ammonium carbonate, filtering, and evaporating the filtrate to dryness. The ammonium β-chloroethanesulphonate, after crystallisation from 95 per cent. alcohol, melted at 194° (corr.) (Kohler, *Amer. Chem. J.*, 1897, **19**, 737, gives 192°) (Found : N = 10·7. Calc., N = 10·5 per cent.).

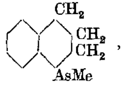
50, CITY ROAD, E.C.1. [*Received, February 14th*, 1921.]

LIII.—*Experiments on the Production of Compounds containing Arsenic as a Centre of Optical Activity.*

By George Joseph Burrows and Eustace Ebenezer Turner.

Michaelis (*Annalen*, 1902, **321**, 159) and Winmill (T., 1912, **101**, 718) showed that certain derivatives of arsenic of the type As(abcd)X could not be obtained in an optically active condition. It appeared, however, to be necessary to attempt the resolution of different types of asymmetric arsenic compounds before concluding that arsenic is peculiar in not functioning as a centre of optical activity in any of its derivatives.

In view of the ease with which the resolution of kairoline oxide was accomplished by Meisenheimer (*Annalen*, 1911, **385**, 117), the authors prepared the compound:



the oxide of which would be the arsenic analogue of kairoline oxide, and, assuming the stereochemical relationships of the valencies of arsenic to be similar to those obtaining in the case of nitrogen, should be capable of resolution. The new arsine, for which the name *As*-methyltetrahydroarsinoline is suggested, is formed when aluminium chloride is allowed to act on γ-phenyl-*n*-propylmethylchloroarsine. Before this ring-closure was attempted, experiments were conducted on the action of aluminium chloride on mixtures of benzene with various chloroarsines, and it was found that, although as stated by Michaelis and others (*Annalen*, 1880, **201**, 184, etc.) the Friedel-Crafts' reaction was not generally applicable in the preparation of arsenic compounds, monochloroarsines were readily converted into tertiary arsines by the reaction in question, phenylmethylchloroarsine, for example, being readily converted into diphenylmethylarsine in the presence of benzene. An interesting case of selective action was observed in this connexion, a mixture of γ-phenyl-*n*-propylmethylchloroarsine and benzene giving no phenylpropylphenylmethylarsine, but only *As*-methyltetrahydroarsinoline.

Owing to lack of material the arsinoline could not be prepared in sufficient quantity to allow an investigation of the oxide and of the hydroxyarsinolinium compounds with active acids.

As a second series, an arsenic analogue of the asymmetric amine-

and phosphine-oxides was studied. The majority of the asymmetric arsine oxides are liquids, and in view of the uncertainty attached to such compounds an endeavour was made to obtain a solid oxide; after many experiments a solid arsine was finally obtained (phenyl-α-naphthylmethylarsine), and from this a well-defined oxide was prepared. It combined readily with *d*-α-bromocamphor-π-sulphonic acid, but the bromocamphorsulphonate obtained in this way gave no indication of being separable into two substances of different rotatory power.

Attention was finally directed to the study of substances of the simple, asymmetric arsonium type. A large number of such compounds were prepared, but two series only were suitable to the investigation.

The first series, derived from the homopiperonylphenyl-α-naphthylmethylarsonium ion, gave indefinite results. The bromocamphorsulphonate could not be obtained free from alcohol of crystallisation, and although on fractionation definite indications of resolution were observed, the authors hesitated to regard this as sufficient evidence for the existence of optically active arsenic derivatives, particularly in view, on the one hand, of the difficulty with which the crystallisation of the bromocamphorsulphonate was attended, and, on the other, of the impossibility of obtaining in the active condition an arsenic compound free from camphor.

The second series, derived from the phenyl-α-naphthylbenzylmethylarsonium ion, gave definite results, one recrystallisation of the bromocamphorsulphonate affording a substance the molecular rotation of which, $[M]_D + 300°$, differed by some twenty units from the rotation of the bromocamphorsulphonic ion (+ 278°); further recrystallisation produced no effect on the molecular rotation. This substance, on treatment with potassium iodide or bromide, was converted into the haloid salt, which had a definite, positive rotation. Racemisation occurred with such rapidity, however, that on no occasion was a molecular rotation of more than 12° (iodide) obtained. Racemisation would appear to occur as the result of the tendency of quaternary arsonium salts to dissociate readily in solution; thus, the iodide of the series in question dissociated in chloroform solution, at least partly, to give benzyl iodide and phenyl-α-naphthylmethylarsine.

The tendency of derivatives of quinquevalent arsenic to break down in solution into derivatives of tervalent arsenic would appear to be more pronounced than the tendency of similar derivatives of nitrogen, and besides affording a possible explanation of the failure of previous workers to obtain optically active derivatives of arsenic, would account for other anomalies observed in the

study of the organic derivatives of this element, such as the properties of the additive compounds described in a previous paper (Burrows and Turner, T., 1920, **117**, 1373), the intramolecular change referred to in the experimental portion of this paper in connexion with the heterocyclic derivative, and also the crystallisation, from solution, of mixtures of quaternary salts as a result of the interaction of an arsine and an alkyl iodide.

EXPERIMENTAL.

γ-Phenylpropyl Alcohol and γ-Bromopropylbenzene.

γ-Phenylpropyl alcohol was prepared by reducing ethyl β-phenylpropionate with sodium and alcohol by Bouveault's method (*Compt. rend.*, 1903, **136**, 1676). The use of absolute alcohol was necessary, as the presence of water in small quantity caused the formation of insoluble sodium salts, which coated the sodium and prevented its dissolution. A solution of ethyl β-phenylpropionate (23·5 c.c.) in 125 c.c. of absolute alcohol was slowly added, under reflux, to a vigorously shaken mixture of small pieces of sodium (19 grams) and broken glass, the last traces of sodium were destroyed by the addition of 50 c.c. of absolute alcohol, and the solution was carefully decomposed with water. The products of several such reductions were united, acidified with hydrochloric acid, neutralised with sodium carbonate, freed from alcohol by distillation and extracted with ether. From the extract phenylpropyl alcohol, b. p. 124—125°/16 mm., was obtained in amount corresponding with a 65 per cent. conversion, whilst by acidifying the extracted solution and again extracting with ether, β-phenylpropionic acid was recovered, the total loss of material amounting to less than 10 per cent. of the initial quantity.

The bromo-compound was readily prepared by Rupe and Bürgin's method (*Ber.*, 1910, **43**, 178).

γ-Phenylpropyldimethylarsine.

(*a*) *Dimethyliodoarsine.*—The following method of preparation is simpler than that described previously (Burrows and Turner, *loc. cit.*).

Arsenious oxide (320 grams), methyl iodide (206 c.c.), and sodium hydroxide (388 grams) were dissolved together in aqueous alcohol. After about twenty hours, the alcohol was removed by distillation and the residue acidified with hydrochloric acid and saturated with sulphur dioxide. The methyldi-iodoarsine that separated (835 grams) was removed, dissolved in 1700 c.c. of alcohol, and

treated with a solution of 408 grams of sodium hydroxide in 600 c.c. of water and with 170 c.c. of methyl iodide. On the next day the alcohol was removed by distillation, and the residue acidified with hydrochloric acid and saturated with sulphur dioxide. The yield of dimethyliodoarsine (435 grams) was 58 per cent. of that theoretically obtainable from the arsenious oxide used.

(*b*) *γ-Phenylpropyldimethylarsine.*—Dimethyliodoarsine (35 grams) dissolved in 100 c.c. of benzene, was slowly added, with shaking, to a Grignard reagent prepared from 40 grams of γ-bromopropylbenzene, 5 grams of magnesium, and 100 c.c. of ether, the mixture finally being heated in warm water for an hour. The formation of an additive compound in considerable quantity necessitated the extraction of the ethereal solution (obtained in the usual manner from the reaction product) with an aqueous solution of sodium hydroxide. The arsine was finally obtained as a colourless, highly refractive liquid, b. p. 133°/14 mm. (Found: As = 32·9. $C_{11}H_{17}As$ requires As = 33·5 per cent.). The yield was 65 per cent. of the theoretical.

The *methiodide* was formed readily, and crystallised from water in colourless needles melting at 144° (Found: I = 34·3. $C_{12}H_{20}IAs$ requires I = 34·7 per cent.).

An *additive* compound, $C_{11}H_{17}As,Me_2AsI$, was formed when the arsine (1 mol.) was mixed with dimethyliodoarsine (1 mol.). It crystallised from ether, methyl alcohol, or even from concentrated hydrochloric acid, and formed colourless prisms melting at 78—81°. It was completely dissociated into its components in benzene solution (Found: I = 27·8; M. [by the cryoscopic method in benzene] 222, 224. $C_{13}H_{23}IAs_2$ requires I = 27·9 per cent.; M. = 456).

γ-Phenylpropyldimethylarsine is the only one of the twelve or more arsines examined that forms an additive compound with dimethyliodoarsine.

Phenylmethyliodoarsine and Phenylmethylchloroarsine.

The method previously described for the preparation of these compounds (Burrows and Turner, *loc. cit.*) has been greatly simplified. A solution containing 365 grams of phenyldichloroarsine, 1200 c.c. of alcohol, 280 grams of sodium hydroxide and 260 grams of methyl iodide, after remaining for one day, was neutralised with hydrochloric acid. The sodium chloride was removed by filtration and the alcohol by distillation, the phenylmethyliodoarsine, which separated to a considerable extent at this stage, was redissolved by adding water, and the solution saturated with sulphur dioxide after the addition of hydrochloric acid. In this way 435 grams

of phenylmethyliodoarsine were obtained. The corresponding chloro-compound was prepared from it by the method previously described.

Conversion of Phenylmethylchloroarsine into Diphenylmethylarsine.

A mixture of 15 grams of the chloro-compound, 60 grams of benzene, and 10 grams of aluminium chloride was gently heated for two hours. Hydrogen chloride was evolved immediately. The product was decomposed with ice and dilute hydrochloric acid, and 7 grams of pure diphenylmethylarsine (identified as the methiodide) were obtained.

γ-Phenylpropylmethylchloro- and -bromo-arsines.

γ-Phenylpropyldimethylarsine (45 grams) was treated in carbon tetrachloride solution with chlorine (1 mol.) dissolved in the same solvent. The pale yellow solution obtained in this way was evaporated and the residue heated at 160—180°, when it decomposed readily with the evolution of methyl chloride, volatile chloroarsines and γ-chloropropylbenzene also being formed in small quantities. The required chloroarsine was obtained (22 grams) as a colourless liquid, b. p. 164—167°/14 mm., when the final residue was distilled under diminished pressure. It could not be obtained free from traces of the original arsine which had been formed by the dissociation of the dichloride into its parent substances (Found: Cl = 13·5. $C_{10}H_{14}ClAs$ requires Cl = 14·5 per cent.).

The corresponding bromo-compound was obtained in a similar manner. The dibromide of the original arsine decomposed readily at 170° and γ-phenylpropylmethylbromoarsine, a colourless liquid, b. p. 177—180°/16 mm., was produced, but it contained traces of dibromoarsine (Found: Br = 28·6. $C_{10}H_{14}BrAs$ requires Br = 27·7 per cent.).

As-Methyltetrahydroarsinoline.

1. *Preparation in Carbon Disulphide Solution.* (*a*) *From γ-Phenylpropylmethylchloroarsine.*—A mixture of the chloroarsine (5 grams), carbon disulphide, and aluminium chloride (2·7 grams) was gently boiled for three hours, when hydrogen chloride ceased to be evolved. The product was decomposed with ice, and the mixture, after being acidified, was extracted with carbon tetrachloride. From the extract, by distillation under diminished pressure, 2 grams of As-*methyltetrahydroarsinoline*, a colourless liquid, b. p. 140°/14 mm., were obtained (*Found*: C = 56·6; H = 5·8; M. [by the cryoscopic method in benzene] 205, 206. $C_{10}H_{13}As$ requires C = 57·7; H = 5·8

per cent.; M. = 208). The difficulty of separating arsines from chloroarsines was again encountered here, and although the boiling point of the substance analysed was quite constant, the preparation of the pure arsinoline from the small quantity of material was impossible. Its constitution, however, is proved by the analysis of its derivatives and by the value of the molecular weight.

As-*Methyltetrahydroarsinoline* is a highly refractive liquid having an odour faintly suggestive of quinoline. It is slowly oxidised in the air and dissolves in concentrated sulphuric acid to give a colourless solution, from which water precipitates the unchanged arsine.

The *methiodide* is readily formed, and crystallises from alcohol or water in colourless prisms melting at 235° (Found: I = 36·1. $C_{11}H_{16}IAs$ requires I = 36·3 per cent.). A hot, alcoholic solution has a yellow colour, which disappears when the solution is cooled. This property is probably due to an intramolecular change,

$$C_6H_4{<}{}^{CH_2\cdot CH_2}_{AsMe_2I-}{>}CH_2 \rightleftarrows C_6H_4{<}{}^{CH_2\cdot CH_2\cdot CH_2I}_{AsMe_2};$$

a rapid estimation of the iodine content with a dilute, alcoholic solution of silver nitrate gave a value 7 per cent. lower than that obtained by the usual analytical method.

The *platinichloride*, obtained in the usual manner, is a yellow, microcrystalline powder melting at 170° (Found: Pt = 23·9. $2C_{10}H_{13}As,H_2PtCl_6$ requires Pt = 23·7 per cent.).

The arsinoline forms other well-defined salts, the *picrate* and the *picrolonate* being yellow, crystalline solids.

(*b*) *From γ-Phenylpropylmethylbromoarsine.*—The bromoarsine (21 grams) was treated in the same manner as the chloro-compound, and gave rise to 10 grams of the arsinoline.

(2) *In Benzene Solution.*—The chloro-arsine (10 grams), when gently heated for three hours with 70 c.c. of benzene in presence of 6·5 grams of aluminium chloride, gave rise to 6 grams of the arsinoline, no phenyl-γ-phenylpropylmethylarsine (see below) being formed.

Phenyl-γ-phenylpropylmethylarsine.

Phenylmethyliodoarsine (88·3 grams) was slowly added to a Grignard reagent prepared from 63 grams of γ-bromopropylbenzene, 10 grams of magnesium, and 300 c.c. of ether. After the usual procedure the final ethereal extract was washed with an aqueous solution of sodium hydroxide to remove the unchanged iodoarsine. The *phenyl-γ-phenylpropylmethylarsine* (60 grams) obtained in this way was a colourless, highly refractive liquid, boiling at 208°/17 mm. (Found: As = 26·1. $C_{16}H_{19}As$ requires As = 26·2 per cent.).

The *methiodide* was formed readily, and crystallised from water

in colourless rhombohedra melting at 102° (Found: I = 29·6. $C_{17}H_{22}IAs$ requires I = 29·7 per cent.).

The *dichloride* was readily formed, but on heating gave a mixture of products, which was not further investigated.

Phenyl-α-naphthylmethylarsine.

This was prepared by the usual procedure. From 117 grams of phenylmethyliodoarsine, 94 grams of α-bromonaphthalene and 14 grams of magnesium in ethereal solution, 102 grams of *phenyl-α-naphthylmethylarsine*, a colourless, crystalline solid, m. p. 58°, b. p. 236—238°/17 mm., were obtained (Found: As = 25·7. $C_{17}H_{15}As$ requires As = 25·5 per cent.). The arsine was readily soluble in ether and crystallised best from alcohol.

The *methiodide* was readily formed on the water-bath and separated from concentrated alcoholic solution in colourless plates melting at 175° (Found: I = 28·9. $C_{18}H_{18}IAs$ requires I = 29·1 per cent.).

Phenyl-α-naphthylmethylarsine Oxide.

The preceding arsine was dissolved in chloroform and bromine (1 mol.; dissolved in chloroform) added, the mixture being well cooled to prevent bromination. The resulting solution was shaken with a slight excess of an aqueous solution of sodium hydroxide, the mixture separated, the chloroform layer washed with water, and then dried and evaporated. After the oxide had once been obtained crystalline, the residue in subsequent experiments became solid at this stage, and after being heated at 120° for a short time (to remove traces of the *dihydroxide*) yielded the oxide in an almost pure state. The latter was crystallised from toluene and formed colourless, well-defined prisms melting at 175° (Found: As = 23·7. $C_{17}H_{15}OAs$ requires As = 24·2 per cent.).

Hydroxyphenyl-α-naphthylmethylarsonium d-*α-Bromocamphor-π-sulphonate.*

The preceding compound, although almost insoluble in ethyl acetate, dissolved immediately in a solution of *d*-α-bromocamphor-π-sulphonic acid (1 mol.) in this solvent, with the evolution of heat. The *bromocamphorsulphonate*, m. p. 161°, being insoluble in cold ethyl acetate, crystallised from the solution on cooling (Found: C = 51·9; H = 5·1. $C_{27}H_{30}O_5BrSAs$ requires C = 52·2; H = 4·9 per cent.). Repeated attempts were made to separate this substance into two diastereoisomerides, but the differences of molecular rotation observed with successive crops of crystals, although

definite, were small and could not be appreciably increased by further fractionation.

A solution of the original bromocamphorsulphonate (0·4963 gram) in 10 c.c. of alcohol, diluted to 50 c.c. with water, gave in a 2-dcm. tube $\alpha_D + 0·89°$; $[M]_D + 278°$. (Silver *d*-α-bromocamphor-π-sulphonate under similar conditions gave $[M]_D + 277°$). When the bromocamphorsulphonate was crystallised from alcohol, or from a mixture of alcohol and ethyl acetate, the first crop of crystals (in several preparations) invariably gave a rotation of $+ 286°$ or slightly higher; for example, a solution containing 0·5210 gram in 50 c.c. of 20 per cent. alcohol gave in a 2-dcm. tube, $\alpha_D + 0·96°$; $[M]_D + 286°$ (Found: C = 52·2; H = 4·9 per cent.).

The results, however, were regarded as insufficient evidence upon which to base the assumption that arsenic was functioning as a centre of optical activity in this compound.

Methylethyliodoarsine.

Ethyldi-iodoarsine (250 grams) was dissolved in a solution of 122 grams of sodium hydroxide in 200 c.c. of water and 600 c.c. of alcohol, and the mixture treated with 75 c.c. of methyl iodide under reflux. Methylation was complete after a few hours, and the solution, having been neutralised and freed from alcohol, was acidified with hydrochloric acid and reduced with sulphur dioxide. The oil that separated was collected, dried, and distilled under diminished pressure, when 138 grams of methylethyliodoarsine, a yellow, oily liquid, b. p. 65°/14 mm., were obtained. It boiled with slight decomposition under atmospheric pressure, spontaneous ignition occurring occasionally (Found: I = 51·2. C_3H_8IAs requires I = 51·6 per cent.).

Phenylmethylethylarsine and Derived Asymmetric Quaternary Compounds.

This arsine was obtained either from the preceding iodo-compound and magnesium phenyl bromide, or from phenylmethyliodoarsine and magnesium ethyl bromide (Burrows and Turner, *loc. cit.*). It combined readily with allyl bromide, homopiperonyl bromide, ω-bromoacetophenone, bromoacetic acid, and benzyl bromide; combination with the last-mentioned substance occurred violently with the formation of a glassy material, which was probably a mixture and could not be crystallised. The same difficulty was encountered with the other compounds.

Phenyl-α-naphthylmethylallylarsonium Bromide.

Phenyl-α-naphthylmethylarsine combined readily with allyl bromide to give a colourless, crystalline compound melting and decomposing at 140° (Found: Br = 18·8. $C_{20}H_{20}BrAs$ requires Br = 19·3 per cent.). It proved unsuitable, however, for conversion into a bromocamphorsulphonate.

Phenacylphenyl-α-naphthylmethylarsonium Bromide.

When phenyl-α-naphthylmethylarsine and ω-bromoacetophenone were warmed together in molecular proportions, a glassy substance was produced, which, in contact with warm alcohol, slowly changed into a bulky, white, crystalline solid melting at 189° (Found: Br = 16·1. $C_{25}H_{22}OBrAs$ requires Br = 16·2 per cent.). It dissolved sparingly in cold alcohol, readily in hot alcohol, and was insoluble in acetone.

The corresponding bromocamphorsulphonate was obtained as a glassy mass which resisted repeated attempts at crystallisation.

Homopiperonylphenyl-α-naphthylmethylarsonium d-α-*Bromocamphor-π-sulphonate.*

Homopiperonyl bromide was prepared by treating homopiperonyl alcohol with twice its weight of hydrobromic acid (saturated at 0°), the use of a larger excess of the acid (Robinson and Robinson, T., 1914, **105**, 1463) being unnecessary.

The bromide combined readily and quantitatively when warmed with a molecular quantity of phenyl-α-naphthylmethylarsine. The *arsonium bromide* was crystallised from alcohol and formed colourless plates melting at 174—175° (Found: Br = 15·7. $C_{25}H_{22}O_2BrAs$ requires Br = 15·7 per cent.).

The bromide was heated in alcoholic solution with the calculated quantity of silver *d*-α-bromocamphor-π-sulphonate, the silver bromide removed, and the filtrate evaporated under diminished pressure. After several days, a crystalline mass of stout needles was obtained. It was, however, impossible to obtain a really suitable solvent for the purpose of fractional crystallisation. The most suitable one was absolute alcohol; very concentrated solutions in this solvent, however, only very slowly deposited crystals, which, moreover, contained alcohol of crystallisation (Found: C = 56·3; H = 5·5. $C_{35}H_{36}O_6BrSAs,C_2H_6O$ requires C = 56·6; H = 5·4 per cent.).

Nevertheless, an attempt was made to separate the substance into two forms by fractional crystallisation from alcohol. The several fractions gave values of $[M]_D$ varying from + 278° to + 300°. On recrystallising a fraction of low rotation, the

molecular rotation could not be increased. Furthermore, it was impossible to obtain the arsonium bromide free from the bromocamphorsulphonate. On mixing an aqueous solution of potassium bromide with a solution of the bromocamphorsulphonate in acetone, an oily precipitate separated, which became crystalline when rubbed, but was contaminated with the bromocamphorsulphonate even after thorough washing.

Phenyl-α-naphthylbenzylmethylarsonium Bromide and d-α-Bromocamphor-π-sulphonate.

Phenyl-α-naphthylmethylarsine and benzyl bromide combined readily on the water-bath to give the *arsonium bromide*, colourless prisms (from alcohol), m. p. 185° (Found: Br = 17·1. $C_{24}H_{22}BrAs$ requires Br = 17·2 per cent.). The bromide was readily soluble in hot alcohol, but dissolved sparingly in cold alcohol, from which it crystallised slowly. Although it was insoluble in water, it dissolved readily in cold dilute alcohol, a fact which can only be explained from the ionic point of view.

When the bromide was treated with the calculated quantity of silver *d*-α-bromocamphor-π-sulphonate in the manner described above, the *bromocamphorsulphonate* was obtained as a glassy mass which became crystalline after remaining for a few days in contact with alcohol and ethyl acetate in a dry atmosphere. It was then found to crystallise from a mixture of alcohol and ethyl acetate, from acetone, or from a mixture of acetone and ether. This bromocamphorsulphonate, unlike the homopiperonyl derivative described above, separated rapidly from its solutions, and the various crops of crystals were analytically identical (Found: C = 58·4; H = 5·3. $C_{34}H_{36}O_4BrSAs$ requires C = 58·7; H = 5·2 per cent.). The original substance formed colourless prisms melting at 187° and was more soluble in a mixture of acetone (or alcohol) and water than in acetone (or alcohol), although it was almost insoluble in water.

The molecular rotation was determined in a 20 per cent. solution of acetone at 20°, parallel determinations being made with silver *d*-α-bromocamphor-π-sulphonate. A solution containing 0·4952 gram in 50 c.c. gave, in a 2-dcm. tube, α_D +0·80°; $[M]_D$ +281° (0·5112 gram of the silver salt gave $[M]_D$ +278°). The bromocamphorsulphonate was then recrystallised once from a mixture of acetone and ether: 0·4984 gram, under the conditions stated above, gave α_D +0·86°; $[M]_D$ +300°. The product obtained in this way, representing less than one-third of the original bromocamphorsulphonate, was then recrystallised four times from the same medium, but suffered no change of rotatory power.

Fresh samples of the bromocamphorsulphonate were prepared from the bromide on several occasions, and the same results were obtained after crystallisation. The authors regard this as evidence *that the arsenic atom is capable of acting as a centre of optical* activity, the arsonium ion in the most active of the bromocamphorsulphonate solutions having $[M]_D + 20°$. Attempts to obtain evidence of the existence of the *l*-arsonium ion were unsuccessful.

d-Phenyl-α-naphthylbenzylmethylarsonium *d*-α-bromocamphor-π-sulphonate has the same melting point as the *dl*-isomeride, which apparently is a pseudo-racemic mixture. When treated in aqueous-acetone solution with an aqueous solution of potassium iodide, the *arsonium iodide* separated in colourless needles melting at 186—187° (Found: I = 24·6. $C_{24}H_{22}IAs$ requires I = 24·8 per cent.). The *d*-iodide is soluble in cold chloroform or in a cold mixture of alcohol and water, also in warm alcohol or warm acetone; solutions in the last two solvents deposit crystals of the inactive iodide after cooling for some time. Solutions of the *d*-iodide in these solvents were examined polarimetrically and in every case a positive rotation was observed, which, although small, was quite definite; the highest molecular rotation obtained was given by a solution prepared by dissolving 1·0258 grams in a warm mixture of 25 c.c. of acetone and 15 c.c. of alcohol, which, after cooling in the absence of nuclei, gave in a 2-dcm. tube, $\alpha_D + 0·10°$; $[M]_D + 12°$. When the *d*-iodide was recrystallised from hot acetone or alcohol, the product was inactive and melted at 183—184°. The melting points of the active and the inactive iodides varied over one or two degrees according to the rate of heating. The observed rotations of solutions in chloroform or in aqueous-alcoholic mixtures were of the order $[M]_D + 5°$.

The *bromide*, prepared in a similar manner as the iodide, gave results of the same type. The *d*-bromide was obtained in colourless crystals melting at 187—188°, but racemisation in solution was rapid and the highest molecular rotation observed was $[M]_D + 5°$.

Formation and Dissociation of Quaternary Arsonium Compounds.

The melting point of the methiodide derived from phenyldiethylarsine has been recorded as 75—77° (Burrows and Turner, *loc. cit.*), and 122° (Michaelis, *Annalen*, 1902, **320**, 296). Methyl iodide and phenyldiethylarsine (the latter prepared from phenyldichloroarsine by the action of either zinc ethyl or magnesium ethyl bromide) have now been allowed to interact under a variety of conditions; the product had a melting point within a few degrees of that previously recorded by us. Products having almost the same

melting point have also repeatedly been obtained from ethyl iodide and phenylmethylethylarsine (prepared from phenylmethyliodoarsine and also from methylethyliodoarsine). The analysis of each of these products agrees approximately with the formula $C_{11}H_{18}IAs$, and it is possible that our products, none of which has a well-defined melting point, are mixtures of one molecular proportion of phenyltrimethylarsonium iodide with two molecular proportions of phenyltriethylarsonium iodide. We have been unable to isolate under any conditions a compound melting at 122°.

Similarly, when phenyldimethylarsine was allowed to react with ethyl iodide, the product varied with the conditions (solvent, temperature, etc.) employed. Thus, on allowing a mixture of the arsine and ethyl iodide in ethereal solution to remain overnight, a very small crop of crystals, m. p. 190°, was deposited. The main product obtained by warming the filtrate on the water-bath, melted at 142°, and was identical with the methiodide of phenyl methylethylarsine (described previously). The product melting at 190° gave $I = 38{\cdot}6$. $PhMe_2EtAsI$ requires $I = 37{\cdot}6$, $PhMe_3AsI$ requires $I = 39{\cdot}2$ per cent. This result is extraordinary, since it involves the replacement of an ethyl group by a methyl group in the presence of an excess of ethyl iodide, and the result can only be explained by assuming that the first product is phenyldimethylarsine ethiodide, which dissociates to form phenylmethylethylarsine and methyl iodide, the latter then combining with unchanged phenyldimethylarsine. On the other hand, the product from phenylmethylethylarsine and methyl iodide always melted at 142°.

In view of these results it seems improbable that quaternary arsonium compounds containing two similar radicles can exist in more than one form. Repeated attempts have been made to throw light upon this question, and each result necessitates the same conclusion. It has been found, for example, that identical products are obtained from α-naphthylmethylethylarsine and methyl iodide and from α-naphthyldimethylarsine and ethyl iodide, and also from γ-iodopropylbenzene and phenyldimethylarsine and from γ-phenylpropyldimethylarsine and methyl iodide. Again, although phenyl-α-naphthylmethylarsine as a rule behaves normally with alkyl haloids, it gives a mixture of products when warmed with ethyl iodide. The results, in fact, recall the work of Pope (T., 1901, **79**, 831; 1912, **101**, 529), and others on quaternary ammoninm salts, except in so far as the latter are apparently far less easily dissociated than the analogous derivatives of arsenic.

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SYDNEY, N.S.W. [*Received, February 17th*, 1921.]

LIV.—*The Action of Alkyl Nitrates on Piperidine.*

By DAVID TEMPLETON GIBSON and ALEXANDER KILLEN MACBETH.

IN a previous paper (Addy and Macbeth, T., 1916, **109**, 754), attention was directed to the action of alkyl nitrites on bases of the pyridine type, and it was seen that the mixing of such compounds led to the formation of the nitrate of the base. As the nitrites were without action on secondary bases, such as piperidine, it seemed of interest to examine the effect of alkyl nitrates in such cases. The results obtained are now recorded.

A mixture of freshly distilled piperidine and *iso*amyl nitrate in a sealed tube will have separated after a few days into two layers. If special care is taken to dry the starting materials thoroughly, no such separation will take place, but after the lapse of three or four days the entire liquid mixture will have become filled with a mass of thin, lustrous plates. The crystals obtained in this way are very deliquescent and are readily soluble in water. They are soluble also in alcohol, but are insoluble in ether or benzene. Traces of water in the solvents are readily taken up by the crystals and they are thus converted into a liquid, from which it is difficult to obtain a solid product again. On this account the substance cannot be recrystallised from alcohol, and the most practical method of purification consists in repeatedly washing the crystals with ether (distilled over sodium) and subsequently drying them in a vacuum oven. The crystals purified in this way melt at 173—174°, and are found to be piperidine nitrate.

Assuming that a mixture of *iso*amyl nitrate and piperidine yields the nitrate of the base, it is possible that the reaction may follow either of two main courses, giving as a second product (*a*) β-methyl-Δ^{β}-butylene (amylene) or alternatively (*b*) amylpiperidine.

$$(a)\ C_5H_{11}{\cdot}NO_3 + C_5H_{11}N = C_5H_{11}N,HNO_3 + C_5H_{10}.$$
$$(b)\ C_5H_{11}{\cdot}NO_3 + 2C_5H_{11}N = C_5H_{11}N,HNO_3 + C_5H_{10}N{\cdot}C_5H_{11}.$$

It may be stated that all the evidence is in favour of the second alternative, as no traces of unsaturated substances have been detected in any of the reactions. Substituted piperidines, on the other hand, have been isolated. This is in agreement with the results of previous work on the action of alkyl nitrates on ammonia. Thus, Juncadella (*Annalen*, 1859, **110**, 255; *Compt. rend.*, 1859, **48**, 342; *J. pr. Chem.*, 1859, [i], 77) has shown that methyl and ethyl nitrates, when heated with ammonia for several days in a sealed tube at 100°, give good yields of methylamine and ethylamine

respectively. Lea (*Chem. News*, 1861, **4**, 71, 88), and Wallach (*Ber.*, 1881, **14**, 422) obtained similar results in the case of ammonia and other nitrates. The formation of substituted piperidines would thus appear to be part of a general reaction of alkyl nitrates on ammonia and partly substituted ammonias.

The nitrates employed in the present work included the ethyl, propyl, *iso*propyl, *n*-butyl, *tert.*-butyl, and *iso*amyl compounds. As some of the experiments were done on a comparatively small scale, the boiling points of the substituted bases were determined by the method described by Siwoloboff (*Ber.*, 1886, **19**, 795), when only small quantities of liquid were available.

iso*Amyl Nitrate and Piperidine.*—This was the first case examined and from the mixture of these compounds very pure piperidine nitrate, melting at 173—174°, was obtained. On treatment with sodium hydroxide it liberated a base which gave a hydrochloride melting at 236° (piperidine hydrochloride melts at 237°). The residue gave the tests for sodium nitrate, and it would thus appear that the solid produced by the action of *iso*amyl nitrate on piperidine is the nitrate of the base. This view is supported by the results of analyses (Found: Nitritic N [nitrometer method] = 9·66; total N = 18·9. $C_5H_{11}N,HNO_3$ requires N = 18·91; nitritic N = 9·45 per cent.).

The results therefore agree with the values required for piperidine nitrate, but Cahours (*Quart. Journ. Chem. Soc.*, 1854, **6**, 175) has described this compound as consisting of needle-shaped crystals prepared by the neutralisation of piperidine with dilute nitric acid, and subsequent concentration. It is evident that the substance described by us could not, on account of its deliquescence, be prepared by this method. All our attempts to prepare piperidine nitrate by neutralisation resulted in the formation of a deliquescent solid agreeing in properties with the substance obtained in the reaction of the base with *iso*amyl nitrate. The neutralisation method, however, does not yield nearly so pure a product.

After removal of the crystals of piperidine nitrate from the reaction mixture of *iso*amyl nitrate and the base, the liquid remaining was fractionally distilled. No distillate was obtained below 100°, and this points clearly to the fact that the reaction takes a course that does not involve the formation of amylene, as this boils at 33° and if present would have been detected in the distillation. A fraction was obtained distilling above 180°, but as considerable charring took place an alternative method of treatment was adopted. The liquid, after the removal of piperidine nitrate, was extracted several times with concentrated hydrochloric acid, and any bases present were thus separated from the excess of *iso*amyl nitrate.

On evaporation, a solid hydrochloride was obtained, which on analysis was found to consist largely of *iso*amylpiperidine hydrochloride (Found: Cl = 19·6. Calc., Cl = 19·1 per cent.). On treatment with sodium hydroxide, the hydrochloride liberates a base, which distils at 187—190°. The base gives a picrate on the addition of a solution of picric acid in ethyl acetate, and the recrystallised picrate melts at 134°. (*iso*Amylpiperidine, b. p. 186°, 188°; *iso*amylpiperidine picrate, m. p. 133°.) As these constants are in agreement with values recorded for *iso*amylpiperidine, it is evident that the base is the substituted piperidine required by the equation already given.

Ethyl Nitrate and Piperidine.—Two parts of piperidine were mixed with rather more than one part of ethyl nitrate and set aside in a closed tube. With thoroughly dry piperidine, the entire liquid was filled with crystals after three or four days at the ordinary temperature. The crystals, after having been separated from the liquid, were purified by the treatment already outlined, and identified as piperidine nitrate by analysis (Found: Nitritic N = 9·34 per cent.).

The liquid remaining after the removal of the piperidine nitrate was fractionally distilled and a final fraction was collected at 124—128°. On treatment with a concentrated solution of picric acid in ethyl acetate this fraction gave a yellow, crystalline picrate melting at 165—167°. Ethylpiperidine boils at 128°, and ethylpiperidine picrate melts at 163° or 167°, according to two different observations. The final fraction in the above distillation is, therefore, evidently ethylpiperidine.

Propyl Nitrate and Piperidine.—In this case also the separation of piperidine nitrate occurred in the usual way in the course of a few days. The filtrate was examined, but as considerable charring took place on distillation, the alternative process, extraction by hydrochloric acid, was adopted. The hydrochloride so obtained gave a free base which distilled at 148—149°. This yielded a picrate, melting at 108°, on treatment with a concentrated, aqueous solution of picric acid. Propylpiperidine boils at 149—150°, and propylpiperidine picrate melts at 108°.

Butyl Nitrate and Piperidine.—The reaction in this case proceeded normally, and the liquid separated from the piperidine nitrate was treated with acid as described in the preceding case. As no reference to butylpiperidine could be traced in the literature, the percentage of chlorine in the hydrochloride, and the amount of platinum in the platinichloride, m. p. 218°, of the base, were estimated (Found: Cl = 20·8. $C_5H_{10}N\cdot C_4H_9,HCl$ requires Cl = 20·1 per cent. Found: Pt = 27·3. $[C_5H_{10}N\cdot C_4H_9]_2,H_2PtCl_6$ requires Pt = 28·1

per cent.). The values obtained show that the base consists largely of butylpiperidine. On treatment of the hydrochloride with an alkali the base was liberated as an oil boiling at 170—172°.

In addition to the cases referred to above, similar results were obtained with *iso*propyl nitrate and *tert.*-butyl nitrate. In all the cases recorded the reaction was allowed to take place at the ordinary temperature, but the change can be accelerated by heating.

Ethyl Nitrate and Diethylamine.—It was thought desirable to extend the work and study the reaction in the case of bases other than piperidine; ethyl nitrate and diethylamine were examined accordingly. The reaction followed the usual course, and after three days the formation of crystals had occurred. The mixture was kept for a few more days to allow the reaction to proceed fully. The liquid was then drawn off from the crystals and examined. Treatment with hydrochloric acid extracted a base, which when liberated by sodium hydroxide distilled at 88° (triethylamine, b. p. 88—89°). The base was converted into the ferrocyanide, in which the percentage of ferric oxide was estimated (*Compt. rend.*, 1902, **134**, 901). Difficulty was experienced in preventing decomposition of the salt, but considering its nature the result was in fair agreement with the theoretical value (Found: $Fe_2O_3 = 36.5$. Calc., $Fe_2O_3 = 38.2$ per cent.). The crystals which separated from the mixture of the nitrate and the base were found to be diethylamine nitrate. This compound is not so deliquescent as piperidine nitrate, but its solubility in the various solvents is of a similar nature. It is soluble in alcohol and in water, insoluble in ether and in benzene. It was purified by solution in alcohol and precipitation by ether. The purified product melted at 100° (diethylamine nitrate, m. p. 99—100°). On treatment with sodium hydroxide a base was liberated which distilled at 53—55° (diethylamine, b. p. 55°). It is therefore evident that the reaction follows the general course, taking place according to the equation:

$$EtNO_3 + 2NHEt_2 = NHEt_2,HNO_3 + NEt_3.$$

From the results outlined above, and the previous work on the action of alkyl nitrates on ammonia, it would appear that the reaction is a general one for the preparation of more highly substituted, aliphatic bases from ammonia or partly substituted ammonias. Solutions of diphenylamine gave no result, but this may probably be attributed to its weakly basic nature. The absence of any reaction in the case of pyridine, quinoline, and bases of this type is doubtless due to the fact that since a tertiary nitrogen atom is present in them there is no possibility of an interchange of the

kind indicated in the typical equations of the reaction formulated above.

We wish to take this opportunity of expressing our thanks to Professor A. W. Stewart for his interest during the course of this work.

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[*Received, January* 31*st*, 1921.]

LV.—*The Friedel-Crafts' Reaction. Part II. Migration of Halogen Atoms in the Benzene Nucleus.*

By MAURICE COPISAROW.

WHILST Part I. of this work (T., 1917, **111**, 10) was devoted to the study of a complex case of a Friedel-Crafts' reaction, the present investigation deals with a case both complex and anomalous. Dumreicher (*Ber.*, 1882, **15**, 1867) found the action of aluminium chloride on bromobenzene to result in the formation of small quantities of benzene, dibromobenzenes, and tarry matter, the greater part of the starting material remaining unchanged. Leroy's work (*Bull. Soc. chim.*, 1887, [ii], **48**, 210) on *p*-bromobenzene followed a similar course. Kohn and Müller (*Monatsh.*, 1909, **30**, 407) obtained small quantities of phenol and bromobenzene by the action of aluminium chloride on a mixture of tribromophenol and benzene. The substitution of toluene for benzene did not alter the character of the reaction (Kohn and Bum, *Monatsh.*, 1912, **33**, 923).

Dumreicher (*loc. cit.*) represented the mechanism of migration by the following equations:

$$\text{I. } C_6H_5Br + Al_2Cl_6 = C_6H_5{\cdot}Al_2Cl_5 + BrCl.$$
$$\text{II. } C_6H_5Br + BrCl = C_6H_4Br_2 + HCl.$$
$$\text{III. } C_6H_5{\cdot}Al_2Cl_5 + HCl = C_6H_6 + Al_2Cl_6.$$

Considering that the existence of bromine chloride is still disputed, and that even if assumed to exist it is certainly unstable under the experimental conditions employed (Bornemann, *Annalen*, 1877, **189**, 206; Delépine and Ville, *Compt. rend.*, 1920, **170**, 1390), we can take it that the essential feature of the reaction is the presence of halogens in a nascent state. This is substantiated by the fact that aluminium chloride has no action on chlorinated hydrocarbons of the aromatic series (Dumreicher, *loc. cit.*; Friedel

and Crafts, *Ann. Chim.*, 1887, [vi], **10**, 413; Kohn and Müller, *loc. cit.*), unless some more reactive substance is present (Friedel and Crafts, *loc. cit.*). However, these observations apparently do not apply to ferric chloride (Thomas, *Compt. rend.*, 1898, **126**, 1213) and hydrocarbons of the ethylene and acetylene series (Delépine and Ville, *loc. cit.*).

The author, studying the action of aluminium chloride on bromo- and *p*-dibromobenzene, found the reaction to be complex, condensation, migration, and pyrogenic-like fission of the benzene nucleus taking place. These three distinctly different reactions form three successive stages, which overlap one another to a considerable extent. Owing to the energetic character of the last two reactions, the ordinary condensation with the formation of bromodiphenyl is greatly inhibited.

The fission of the benzene nucleus with the formation of carbon, bromo-derivatives of naphthalene, anthracene, etc., is favoured by extreme conditions of temperature and concentration of aluminium chloride.

Whilst owing to the complexity of the reaction there can be no question of an equilibrium, in its strict sense, a qualitative application of the law of mass action is possible with advantage to the elucidation of the problem.

Examining the equations set forth above as representing the course of migration of the halogen atoms, we see that the nascent bromine may attack, not only the starting material, that is, the bromobenzene, but also the products, the dibromobenzenes and benzene, probably the latter in preference, thus not only retarding, but actually reversing the reaction. This, combined with the enhanced fission caused by the prolonged action of the aluminium chloride, resulted in the case of previous investigations in low values, the yield of the products of migration being 5 to 7 per cent. of the theoretical, calculated on the basis of the equation: $2C_6H_5Br = C_6H_6 + C_6H_4Br_2$.

In the course of the present research it was found that the migration of the bromine atom, as estimated by the formation of benzene, could be increased to 83 per cent. of the theoretical by:

(1) Ensuring the continuous removal of benzene, immediately it was formed, from the sphere of reaction, and

(2) Carrying out the reaction in a current of hydrogen chloride or hydrogen.

The efficiency of the hydrogen chloride and hydrogen appears to represent the combined effect of the chemical and mechanical actions, as the employment of such an inert gas as nitrogen resulted in a certain improvement in the yield of benzene, although

a good deal below that obtained in the case of the gases previously mentioned.

An attempt to use phenol for the purpose of fixing the nascent bromine, and so facilitating the progress of migration, met with but partial success, owing to the great reactivity of phenol with aluminium chloride. However, the formation of tribromophenol and the almost complete disappearance of dibromobenzenes were sufficient to show the validity of the anticipated effect.

In addition to benzene and its bromo-derivatives, the reaction product was found to consist of traces of bromodiphenyl and bromo-derivatives of naphthalene and anthracene, these substances being identified indirectly through their products of oxidation.

Whilst the action of aluminium chloride on bromo-derivatives of benzene is definite and energetic, aluminium chloride and aluminium bromide have no such effect on chloro- and bromo-derivatives of benzene respectively. The action of aluminium bromide on chloro-derivatives of benzene is very feeble.

It is clear from these observations that in order to avoid side-reactions in Friedel-Crafts' condensations, in which halogen derivatives of benzene are to be employed, chloro-derivatives of benzene must be used with aluminium chloride.

EXPERIMENTAL.

[With CYRIL NORMAN HUGH LONG.]

Experiment I.—A mixture of bromobenzene (2 parts) and finely powdered aluminium chloride (1 part), when heated on the steam-bath for eight hours under reflux (with mechanical stirring), gradually assumed a dark red colour, solid matter was deposited, and hydrogen chloride and some hydrogen bromide were evolved. The reaction-mixture was treated with ice and a little hydrochloric acid and then distilled in a current of steam.

The red oil obtained in the distillate was dried over sodium sulphate and fractionally distilled, the following fractions being collected:

(1) Below 100°; (2) 100—185°; (3) above 185°.

The first and the second fractions contained benzene and bromobenzene respectively. The fraction of high b.p. deposited after some time crystals of *p*-dibromobenzene (identified by the method of mixed m. p.). These were separated and the mother liquor again fractionated, when the bulk distilled at 217—218°, and was proved, in agreement with Dumreicher (*loc. cit.*) and Leroy (*loc. cit.*), to consist of *o*-, *m*-, and a little *p*-dibromobenzene. The small residue solidified on keeping. It was separated by fractional crystallisation

from alcohol into 1 : 3 : 5-tribromobenzene, m. p. 117°, and 1 : 2 : 4-tribromobenzene, *m. p.* 44°.

The dark, tarry residue left after steam distillation was freed from water and extracted with glacial acetic acid to separate the carbonaceous matter, and the extract was treated with chromic acid as in the case of the oxidation of anthracene. The reaction-mixture was poured into water, the mass made alkaline to litmus, and filtered. The residue crystallised from benzene in yellow needles melting at 188°, and was proved to be 1-bromoanthraquinone. The identity was confirmed by fusing the product with potassium hydroxide, when 1-hydroxyanthraquinone was formed, and not alizarin (which is produced from 2-bromoanthraquinone by this treatment). The alkaline filtrate was concentrated, cooled, acidified with hydrochloric acid, and immediately extracted with chloroform. From the extract *p*-bromobenzoic acid, m. p. 251°, was isolated. The solid remaining suspended in the acidified, aqueous solution after the extraction with chloroform was filtered off, fractionally crystallised from water, and sublimed. It was thus found to consist of 4-bromophthalic anhydride and a little 3-bromophthalic anhydride.

These products of oxidation indicate that the reaction-products consist, in addition to benzene and its bromo-derivatives, of bromo-derivatives of diphenyl, naphthalene, and anthracene.

The yield of benzene in this reaction was found to be 7 to 8 per cent. of the theoretical. The yield of dibromobenzenes approached that of benzene, although no strict relationship in yield, such as was assumed by Dumreicher (*loc. cit.*), could be detected, especially in the experiments to be described. The yield of the other products of reaction was but small.

When the experimental conditions were altered by increasing the temperature of reaction and the quantity of aluminium chloride, or by passing a current of dry hydrogen chloride through the mixture during the reaction, the yield of benzene and of dibromobenzenes was decreased, and that of the brominated anthracene, as indicated by the amount of oxidation products, increased. The residue was dark brown or black, the quantity of unchanged bromobenzene was considerably decreased, and the amount of carbonaceous matter greatly increased. In the product obtained by oxidising the residues very little bromophthalic acid and no bromobenzoic acid could be detected.

At a lower temperature of reaction, with a smaller proportion of aluminium chloride or in the presence of a volatile solvent such as carbon disulphide, the reaction was feeble and the yields poor. The employment of benzene as a solvent had no marked effect on the course of the reaction.

Experiment II.—A mixture of bromobenzene (4 parts) and finely powdered aluminium chloride (1 part) contained in a distillation flask was heated in the steam-bath for eight hours, until benzene almost ceased to distil. The reaction was accompanied with the evolution of hydrogen chloride and hydrogen bromide, and the distillate was found also to contain some bromobenzene carried over by the benzene vapour. The product was worked up as in the previous experiment. The yields of benzene and of unchanged bromobenzene were 26 per cent. and 40 per cent., respectively, and the yield of dibromobenzenes was slightly lower than that of benzene.

Experiment III.—This experiment was carried out under conditions similar to those employed in the previous experiment, with the difference that a current of dry nitrogen was passed through the mixture during the whole course of the reaction.

The yield of benzene and of dibromobenzenes was found to be increased, the former being 42 per cent. of the theoretical.

When dry hydrogen chloride was substituted for the nitrogen the yield of benzene was 78 per cent. of the theoretical, and that of dibromobenzenes 70 per cent., whilst with dry hydrogen the yield of benzene increased to 83 per cent., and that of dibromobenzenes decreased to 67 per cent., 10·5 per cent. of bromobenzene being recovered unchanged. The quantity of fission products and carbonaceous matter was small.

The quantity of tribromobenzenes, though small, increased with the yield of dibromobenzenes, the amount of 1 : 3 : 5-tribromobenzene being considerably in excess of that of the 1 : 2 : 4-isomeride.

In the experiment with hydrogen, a marked increase in the evolution of hydrogen bromide was noted. The gases were passed at the rate of three bubbles per second, since some benzene was lost when a rapid current was used and some bromobenzene was carried over with the gases.

Experiment IV.—The interaction of bromobenzene (12 parts), phenol (4 parts), and aluminium chloride (3 parts) was allowed to proceed under conditions identical with those described in experiment III. No carbonisation took place; the small residue left after the distillation with steam was soluble in alkalis and proved to be tribromophenol. The yield of benzene (reaction in presence of hydrogen chloride) was 35 per cent. of the theoretical, but only traces of dibromobenzenes were formed. This experiment indicates even more clearly than the last experiment (in presence of hydrogen) the possibility of modifying the course of migration of the halogen atoms by the introduction of substances sensitive to halogens. The considerable reactivity of phenol and aluminium chloride exerts however, an inhibiting effect on this reaction.

Experiment V.—When chlorobenzene was heated with aluminium bromide under the various conditions described in the previous experiments the only effect observed was a slight reddening of the mixture, minute red globules appearing on the surface of the aluminium bromide. In the presence of hydrogen chloride, bromine was evolved in small quantity, the chlorobenzene remaining unchanged.

Aluminium chloride and aluminium bromide did not react with chlorobenzene and bromobenzeno respectively under any of the conditions described above.

Experiment VI.—23·6 Grams of *p*-dibromobenzene were heated with 5·9 grams of powdered aluminium chloride for eight hours in a current of dry nitrogen, the conditions being those described in experiment III. The reaction was accompanied with an evolution of hydrogen chloride and hydrogen bromide, and the mixture acquired a viscous, tarry consistence. The product after treatment with ice and a little hydrochloric acid was distilled in steam. The white solid that was deposited in the condenser towards the end of the distillation proved to be 1 : 3 : 5-tribromobenzene.

The oily portion of the distillate was dried and fractionally distilled, the following fractions being collected:

Below 185°, 2·5 grams (partly in the receiver during the reaction).

185—225°, 8·0 grams (partly solid).

Above 225°, 7·1 grams (liquid and solid).

The first fraction contained bromobenzene and a little benzene, the second the isomerides of dibromobenzene (proved by Leroy's method), and the last mainly 1 : 3 : 5- and a little 1 : 2 : 4-tribromobenzene.

The residue (2 grams) was extracted with a little alcohol, and from the solution a white, crystalline product having no definite melting point separated after some time, which appeared to be a mixture of tri- and tetra-bromobenzenes. 1-Bromoanthraquinone was isolated from the residue after it had been oxidised with chromic acid.

When the percentage of aluminium chloride was increased, the temperature raised, or a current of hydrogen chloride or hydrogen passed, the reaction became more vigorous, the yield of mono- and tri-bromobenzenes and of carbonaceous matter being increased.

In conclusion, the author wishes to express his best thanks to Prof. A. Lapworth for the interest he has taken in this work.

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MANCHESTER. [*Received, January 26th, 1921.*]

LVI.—*The Chlorovinylchloroarsines.*

By Stanley Joseph Green and Thomas Slater Price.

Following the announcement by Pope, that ethylene is absorbed by the chlorides of sulphur, forming ββ′-dichlorodiethyl sulphide (communications to the Chemical Warfare Department, since published in T., 1920, **117**, 271), it occurred to the present authors that the action of acetylene and ethylene upon other inorganic, anhydrous chlorides was worthy of investigation. Acetylene and ethylene were therefore passed into the liquid, anhydrous chlorides of arsenic, antimony, and tin, at temperatures varying up to their boiling points, and at pressures of the gas varying up to four atmospheres. In each case a little absorption of the gas occurred. After a short time, however, absorption ceased and the solution on boiling completely surrendered the gas. Little, or no, chemical action therefore occurred.

Shortly after the completion of these experiments the American Chemical Warfare Service announced that in the presence of anhydrous aluminium chloride arsenic trichloride absorbs acetylene, forming a highly vesicant product. The yields obtained were low, but the reaction evidently deserved further study. We therefore repeated our former experiments, using acetylene and anhydrous arsenic trichloride, with anhydrous aluminium chloride as catalyst, with the result that three compounds, probably represented by the following constitutional formulæ, were isolated in a pure state.

β-Chlorovinyldichloroarsine, $CHCl{:}CH{\cdot}AsCl_2$.

ββ′-Dichlorodivinylchloroarsine, $(CHCl{:}CH)_2AsCl$.

ββ′β″-Trichlorotrivinylarsine, $(CHCl{:}CH)_3As$.

Dafert (*Monatsh.*, 1919, **40**, 313), from the product of the reaction between acetylene and arsenic trichloride in the presence of aluminium chloride, has isolated a compound, to which he assigns the formula $AsCl_3,2C_2H_2$, the composition and the properties of which correspond with those of dichlorodivinylchloroarsine.

Homologues of the chlorovinylchloroarsines would appear to have been prepared (D.R.-P. 296915, 1918) by using higher hydrocarbons of the acetylene series. No details are given, however, and no catalyst is mentioned.

Experimental.

Commercial acetylene, partly purified by passage through concentrated sulphuric acid, was bubbled through a well-shaken, water-cooled mixture of 440 grams of anhydrous arsenic trichloride and 300

grams of anhydrous aluminium chloride. Absorption was rapid, much heat being developed. After six hours 100 grams of acetylene had been taken up, yet absorption was still taking place readily. The reaction mixture had increased considerably in volume, was dark coloured and viscid, and had developed a very powerful odour, suggestive of pelargoniums.

If this product is allowed to stand, spontaneous decomposition eventually commences, even at the ordinary temperature, and the heat of decomposition may so augment the reaction that it ultimately becomes very violent. Attempts to distil this crude product always led to violent explosions. The reaction mixture, which evidently contained an unstable compound of aluminium, was therefore immediately decomposed by being poured into an ice-cold solution of hydrochloric acid,* of constant boiling point strength, whereby considerable heat was developed. The oil that separated, consisting of a mixture of unchanged arsenic trichloride and the three chlorovinylchloroarsines, was distilled in a current of vapour from hydrochloric acid of constant b. p., and the oil obtained in the distillate was separated and fractionally distilled under diminished pressure. After three fractionations there were obtained:

I. 137 Grams of unchanged arsenic trichloride.

II. 47 Grams of a liquid, b. p. 93°/26 mm.

The American report gave b. p. 96°/30 mm., and analyses, iodine absorption, and molecular-weight determinations indicated that the substance was chlorovinyldichloroarsine. The properties of the compound obtained by us agreed with those described in the American report, so that there is no doubt as to its identity (Found: Cl = 51·41; 50·9. $C_2H_2Cl_3As$ requires Cl = 51·30 per cent.).†

Dafert obtained a small quantity of a "stinking heavy liquid" as an intermediate fraction between arsenic trichloride and his compound $AsCl_3,2C_2H_2$, but he does not appear to have submitted it to further investigation; it probably contained chlorovinyldichloroarsine.

III. 44 Grams of a liquid, b. p. 130—133°/26 mm. This was found to be dichlorodivinylchloroarsine (Found: As = 31·1; Cl = 45·65. $C_4H_4Cl_3As$ requires As = 32·12; Cl = 45·58 per cent.), and is doubtless identical with the compound obtained by Dafert.

* Hydrochloric acid, as originally recommended by the American Chemical Warfare Service, is much more satisfactory than water (Dafert, *loc. cit.*), since the latter causes extensive decomposition of arsenic trichloride, with precipitation of arsenious oxide, rendering the solution difficult to manipulate.

† It should be stated that these compounds were not submitted to a detailed chemical investigation, since that was not the immediate object in view.

IV. 164 Grams of a liquid, b. p. 151—155°/28 mm. This was shown to be trichlorotrivinylarsine (Found: As = 28·2; Cl = 41·7. $C_6H_6Cl_3As$ requires As = 28·89; Cl = 41·01 per cent.).

The arsenic chloride fraction tended to become dark brown and finally black on keeping for a short time, whilst the chlorovinyldichloroarsine fraction quickly became purple, then dark, and finally black. As purification became more complete, however, these changes of colour became more gradual, and the pure materials remained colourless for a long time. Samples prepared more than a year ago, and kept in the dark, are now only pale brown. The total percentage yield, calculated from the amount of arsenic trichloride entering into reaction, is 64·9, and the yield calculated from the acetylene used is 66·6 per cent. of the theoretical.

Since it had been found that considerable heat was developed in the reaction between acetylene, arsenic trichloride, and aluminium chloride, and that an unstable, intermediate product was apparently formed, the effect of a solvent was tried, in the hope that it would enable the reaction more easily to be controlled. A mixture of arsenic trichloride (440 grams) and aluminium chloride (300 grams) was diluted with an equal volume of carefully dried carbon tetrachloride, and acetylene, purified as before, passed in. The reaction mixture was well shaken and the temperature kept below 15°. Absorption of acetylene appeared to be as rapid as when the solvent was absent. The aluminium chloride gradually became replaced by a viscous, straw-coloured oil, which was doubtless the unstable, intermediate compound of aluminium, the formation of which had already been inferred from the properties of the product of the previous reaction; if the temperature was allowed to rise, the straw-coloured substance blackened and showed all the signs of decomposition.

After acetylene had been passed for six hours, the product was decomposed and then distilled as before. The lower layer of the distillate, on fractionation, yielded 126 grams of unchanged arsenic trichloride, 19 grams of chlorovinyldichloroarsine, 56 grams of dichlorodivinylchloroarsine, and 204 grams of trichlorotrivinylarsine, a yield of 64·6 per cent. calculated on the amount of arsenic trichloride used.

In further experiments, with the object of increasing the formation of chlorovinyldichloroarsine, amounts of acetylene were used corresponding with the formation of the primary chloroarsine. Arsenic trichloride (440 grams) and aluminium chloride (150 grams), diluted with an equal volume of carbon tetrachloride, were treated with 50 grams of acetylene, as before. The products, separated in the usual way, consisted of unchanged arsenic trichloride (271

grams), chlorovinyldichloroarsine (71 grams), dichlorodivinylchloroarsine (46 grams), and trichlorotrivinylarsine (60 grams), the yield obtained being 82·8 per cent. calculated on the arsenic trichloride used, and 74·6 per cent. on the acetylene.

The experiments described show that the secondary and tertiary chloroarsines tend to form very easily, and at the expense of the primary. Thus, in two experiments where a considerable proportion of acetylene was absorbed, the main constituents of the product were unchanged arsenic trichloride and the tertiary arsine. In the third experiment, where the amount of acetylene absorbed was limited, the tertiary compound was still formed in large quantity, whilst more than half of the arsenic trichloride remained unchanged. Clearly the rate of reaction of acetylene increases as chlorovinyl radicles become attached to the arsenic atom. This may be due to the fact, already mentioned, that when acetylene is passed into the mixture of arsenic trichloride and aluminium chloride, the aluminium chloride becomes replaced by and embedded in a viscid straw-coloured oil, which is regarded as the unstable, intermediate compound of aluminium, and this tends to withdraw arsenic trichloride, but not the primary products of reaction, from contact with aluminium chloride.

Varying the relative proportions of arsenic trichloride and aluminium chloride between wide limits produced little, if any, difference in the course of the reaction. Anhydrous ferric chloride behaved similarly to aluminium chloride, but was not so active.

Properties of the Chlorovinylchloroarsines.

β-*Chlorovinyldichloroarsine*, $CHCl{:}CH{\cdot}AsCl_2$, is a colourless or faintly yellow liquid boiling at 93°/26 mm., or 96°/30 mm. Under certain conditions, especially if impure, this compound changes in colour to a fine purple, deepening into black. A small quantity, even in very dilute solution, applied to the skin causes painful blistering, its virulence in this respect approaching that of dichlorodiethyl sulphide. It is also a very powerful respiratory irritant, the mucous membrane of the nose being attacked and violent sneezing induced. More prolonged exposure to the vapour leads to severe pain in the throat and chest.

The substance is insoluble in water or dilute acids, but soluble in all the common organic solvents. A dilute solution of an alkali hydroxide, even when cold, causes a vigorous reaction, acetylene being evolved with brisk effervescence. Halogens are rapidly absorbed with the formation of a variety of products. Thus, if a dilute solution of bromine in carbon tetrachloride be added slowly

to a solution of the chloroarsine in the same solvent, the colour of the bromine slowly disappears, and on shaking, or on keeping, fine leaflets of a bromo-compound separate, melting at 122°.*

ββ'-Dichlorodivinylchloroarsine, $(CHCl{:}CH)_2AsCl$, is a colourless, or pale yellow liquid, boiling at 130—133°/26 mm. Dafert gives the b. p. as 108°/7 mm. and 250°/atm. When free from the primary chloroarsines it remains colourless for a long time. Applied to the skin, the substance has vesicating properties, but is much less powerful in this respect than chlorovinyldichloroarsine. Its irritant properties on the respiratory system, on the other hand, although similar to those of chlorovinyldichloroarsine, are much more intense.

Dichlorodivinylchloroarsine is insoluble in water and dilute acids, but soluble in all proportions in the common organic solvents. Halogens are rapidly absorbed with the formation of additive compounds. For purposes of identification the product of oxidation with concentrated nitric acid is most convenient. A few drops of dichlorodivinylchloroarsine are gently warmed with an equal volume of concentrated nitric acid. Brown fumes are evolved, and on cooling and keeping, colourless crystals separate, which melt at 97°.

ββ'β''-Trichlorotrivinylarsine, $(CHCl{:}CH)_3As$, is a colourless liquid, boiling at 151—155°/28 mm. On keeping for several weeks, little or no change in colour takes place. Immersed in ice-water it readily solidifies to an ice-like mass, the freezing point being 3—4°, the solid remelting at the same temperature.

Trichlorotrivinylarsine is neither a strong vesicating agent nor a powerful respiratory irritant. At the same time, its odour is pungent and most unpleasant, and induces violent sneezing. It is insoluble in water, dilute acids, and in rectified spirit. In the last respect it differs from the primary and secondary chloroarsines, both of which mix in all proportions with rectified spirit. It is therefore easily and completely purified by shaking repeatedly the roughly fractionated liquid with alcohol, separating, distilling, and finally freezing. With the exception of alcohol, it is soluble in all the common organic solvents. Halogens are readily absorbed, with formation of definite compounds, but the simplest tests depend on its slight solubility in alcohol and its freezing point.

Action of Arsenic Trichloride on the Chlorovinylarsines.

When pure trichlorotrivinylarsine is heated with arsenic trichloride at 200—220°, a mixture of arsenic trichloride with all

* Since it was not our object at that time to investigate halogen derivatives, no attempt was made at their identification. They were merely employed as means for characterising the chlorovinylchloroarsines.

three arsines is obtained. The proportion of these four compounds in the resulting mixture naturally depends on the proportions of the starting materials.

Mixtures of arsenic trichloride and trichlorotrivinylarsine were heated in a sealed tube at 220° for four hours, and the contents then fractionated. The results of two experiments were as follows, the figures given being weights in grams.

Tertiary arsine used.	Arsenic trichloride used.	Arsenic trichloride in product.	Primary chloroarsine formed.	Secondary chloroarsine formed.	Tertiary arsine in product.
81·5	67·5	23·6	50·0	61·6	little
56·8	79·2	34·8	65·5	22·1	little

No decomposition was ever noticeable. In the two experiments, the yields of pure products represent 88 per cent. and 91 per cent. respectively of the starting materials. Since losses are inevitable in fractionating such small quantities of liquids, it may be concluded that the reactions expressed by the following equations proceed quantitatively:

$$(CHCl{:}CH)_3As + 2AsCl_3 = 3CHCl{:}CH{\cdot}AsCl_2,$$
$$2(CHCl{:}CH)_3As + AsCl_3 = 3(CHCl{:}CH)_2AsCl.$$

Conclusions.—Three compounds are formed when acetylene acts upon arsenic trichloride in the presence of aluminium chloride. These compounds, in composition and in chemical properties, correspond with the three possible chlorovinylchloroarsines. Usually trichlorotrivinylarsine is the main product, but this can be easily and quantitatively changed to a mixture of the primary and secondary chloroarsines by heating at 200—250° with arsenic trichloride.

Acknowledgments.—The authors are indebted to the Lords of the Admiralty, and to the Chemical Warfare Section of the Directorate of Artillery, War Office, for permission to publish this account of work carried out while serving at the Royal Naval Experimental Station, Stratford, London, E. We also wish to accord grateful recognition to a number of chemists, who, as service subordinates, assisted us in carrying out some of the experiments connected with this investigation. In particular, we would mention Messrs. H. D. K. Drew, M.Sc., W. S. Ritchie, B.Sc., and J. A. Stevenson.

[*Received, August* 19*th*, 1920.]

LVII.—*The Determination of the Sorption of both Solvent and Solute. Part I. Preliminary. The System : Benzene–Iodine–Charcoal.*

By Abu Mohamed Bakr and Joseph Edgar King.

It has long been known that the excellent empirical formula for sorption, $\frac{x}{m} = kc^{\frac{1}{n}}$, cannot be susceptible of general application. Experimental results have always been obtained by shaking a certain volume of a solution of known strength with a known amount of sorbing material such as charcoal, and analysing a sample of the remaining solution. The calculation is then based upon the assumption that the solvent has remained unaffected by the charcoal, so that any change in concentration observed is ascribed to sorption of the solute. It is clear, however, that if, for example, both solvent and solute are sorbed by carbon in the same proportion as that in which they occur in the solution, the analysis would indicate no change, and therefore no sorption, even if the latter was very great. Thus from a purely practical point of view the implied definition of sorption hitherto has been change in concentration rather than change in total amount of solute remaining in solution.

Although Freundlich had discussed such considerations in 1907, no method has been suggested of accurately analysing the apparent sorption, which is merely relative, into its two absolute components. Williams in 1914 (*Medd. K. Vetenskapsakad. Nobel-Inst.*, **2**, No. **27**, 23 pp.), and, independently, Osaka (*Mem. Coll. Sci. Kyōtō*, 1915, No. **6**) attempted to introduce a correction for the sorption of the solvent by carrying out blank experiments in which the charcoal was exposed to the saturated vapour of pure water until the weight of the former no longer increased. They then calculated the results of sorption experiments carried out in the usual way by assuming that the same weight of water was sorbed in all experiments with aqueous solutions at the same temperature.

This procedure is open to grave objection in that, first, the vapour of the solvent, if saturated, is known to condense in liquid form, filling all the pores and capillaries of the charcoal, and, secondly, it is also known that the sorption of each of two substances is influenced by the presence of the other, although there are very few quantitative measurements of this interfering effect. (See, for instance, Bancroft, *J. Ind. Eng. Chem.*, 1921, **13**, 83, who on behalf of a Committee of the National Research Council urges that such investigation be undertaken.) It is shown below that sorption of

benzene may be almost halved in the presence of iodine in sufficient quantity.

The present paper describes a general method of determining the true sorption from solutions suggested by Professor J. W. McBain some years ago, which is here applied in a preliminary manner to the case of iodine solutions, for which there exists an abundance of relative measurements.

The method consists in exposing the carbon to the vapour of the solution and likewise to that of the pure constituents, so that equilibrium is attained through the vapour phase. The objection with regard to condensation of liquid in the capillaries and pores of the sorbing agent is obviated by keeping the latter at a temperature far above that of the liquid with the vapours of which it is in equilibrium. It is soon realised that this is adequate, since values are obtained which within wide limits of pressure are independent of the relative temperatures of the liquid and of the sorbing agent. It is also easily possible to test the equilibria by "reverse" experiments in which the solutions are initially placed in contact with the sorbing agent and are then allowed to distil over to the receiver at the lower temperature. Developments readily suggest themselves and will be described in Part II. The methods are applicable in full only to cases in which solvent and solute are almost equally volatile.

EXPERIMENTAL.

Two specimens, I and II, of charcoal were prepared by strongly heating ground beechwood charcoal for five hours in an evacuated, silica flask. The charcoal was allowed to cool in the vacuum, and was then transferred to stoppered bottles and kept in a desiccator.

The iodine was sublimed from its mixture with potassium iodide and resublimed, and the product was dried in a greaseless desiccator. Kahlbaum's benzene free from thiophen was used.

Numerous forms of apparatus were employed in this preliminary work; the final form is shown in *Figure 1*.

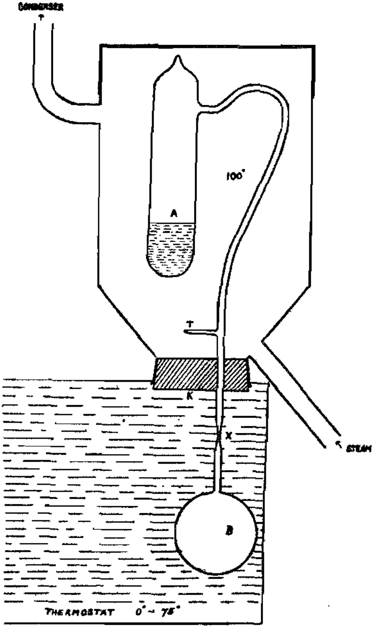
The vessel, A, of about 50 c.c. capacity, containing the charcoal was connected with the receiver, B (20 c.c.), as shown. The thick-walled, glass tube, T, the aperture of A, and the tube connecting A with B were drawn out to facilitate quick sealing.

The vessel A was kept at 100° by means of a steam jacket fitted to act as a reflux condenser. In later experiments an electric oven has been used and the T-joint in A made at the neck instead of the side.

The temperature, and therefore the vapour pressure, of the liquid in B were kept constant during any one experiment by

immersing the receiver in a thermostat. In a "reverse" experiment a weighed quantity of the charcoal was delivered into A by means of a long-necked weighing-bottle, 10 c.c. of the solution were

FIG. 1.



added from a pipette, and A was sealed off. The contents of A were frozen by a mixture of solid carbon dioxide and ether and the whole apparatus was evacuated by means of a Toepler pump attached to T, which was then sealed off. Earlier experiments showed this evacuation to be necessary; thus in one case,

when air was present, only 1—2 c.c. of benzene distilled from A at 100° to B at 25° in four days.

The apparatus was held in position in the steam jacket by a split cork, K, the joint being made water-tight with a plasticine preparation. When steam was admitted into the jacket the unsorbed liquid in A quickly distilled over to B, usually in five to ten minutes, and great care was required to prevent frothing and the consequent carrying over of charcoal to the receiver. After the violent ebullition had ceased and the charcoal was apparently dry the lid of the steam jacket was fitted on and the current of steam continued for twenty hours. The bulb B was then sealed off at X.

If v is the volume of the free space in A, the weight of charcoal, iodine, and sorbed benzene is given by $w - a$, where w is the weight (corrected for displacement of air) of the contents of A at the conclusion of the experiment and a is the weight of v c.c. of benzene vapour at 100° and a pressure, p, determined by the temperature of B (the vapour pressure of iodine is negligihle in comparison with p). The weight of the iodine is the difference between the amount present in the original solution and the amount estimated by titrating the final contents of B.

In the tables x is the weight of benzene sorbed by m grams of charcoal. Each experiment was done in duplicate.

Sorption with Pure Benzene.

TABLE I.

Sorption of Benzene Vapour by Charcoal I at 100°.
"*Reverse*" *Experiment.*

Temp.	Pressure in mm.	m.	x.	x/m.	Mean x/m.
75°	650	1·1682	0·4282	0·37	0·37
,,	,,	1·5284	0·5648	0·37	
25°	95	1·2476	0·4767	0·38	0·36
,,	,,	1·2944	0·4390	0·34	
0°	26·5	1·3831	0·4085	0·30	0·30

When these results are plotted with the theoretical value of zero sorption for zero pressure of benzene, the sorption curve for benzene vapour should be obtained, but the three points lie close together on a nearly flat part of the curve, so that the constants in Freundlich's formula

$$\frac{x}{m} = kp^{\frac{1}{n}}$$

are not accurately obtained. At the pressures employed in these

experiments a saturation value for the sorption of the benzene is reached.

TABLE II.

Sorption of Benzene Vapour at 25° by Charcoal II at 100°.
(Equilibrium from Both Sides).

Method.	Time.	*m.*	*x.*	*x/m.*	Mean *x/m.*
Direct	3 days	1·0540	0·3169	0·300	0·295
,,	3½ ,,	1·1352	0·3286	0·289	
Reverse	20 hours	1·0233	0·2894	0·283	0·287
,,	20 ,,	1·0708	0·3121	0·291	

Hence results obtained in twenty hours by the reverse method represent a state of true equilibrium in the case of pure benzene.

Sorption of Benzene containing Iodine.

In the first series of experiments, in which the "reverse" method was employed, *A* contained originally 10 c.c. of *N*/5-solution of iodine in benzene, together with various amounts of charcoal at 100°, the lower thermostat being kept at 25°. The results are given in Table III.

TABLE III.

Sorption of Benzene from Iodine Solutions by Varying Amounts of Charcoal I.

m.	Iodine in *B* (gram).	*x.*	*x/m.*
0·5002	0·031	0·121	0·24
1·0013	0·010	0·248	0·25
1·0002	,,	,,	,,
1·5004	0·001	0·375	,,
1·5008	,,	0·374	,,
1·9996	trace	0·506	,,

In the second series the weight of charcoal was kept at about 1 gram and the concentration of iodine was varied from 0·1*N* to 0·4*N*. As before, the temperatures of *A* and *B* were 100° and 25° respectively.

TABLE IV.

Sorption of Benzene from Iodine Solutions of Various Concentrations by Charcoal I. "Reverse" Method.

Time (days)	*m.*	Iodine in *A* (gram).	Iodine in *B* (gram).	*x.*	*x/m.*
1	0·9934	0·1253	0·0028	0·3004	0·30
1	1·2764	0·2505	0·0104	0·3122	0·25
1	1·0738	0·4898	0·0510	0·2410	0·22
4	1·0980	0·4843	0·0504	0·2531	0·21

A "direct" experiment, in which 10 c.c. of a solution containing

0·1244 gram of iodine were placed in *B* (25°), and a specimen of charcoal II in *A* (100°), gave the following result :

Time (days).	*m*.	Iodine in *B* (gram).	*x*.	*x*/*m*.
3½	1·4124	0·1241	0·384	0·27

Whilst with pure benzene equilibrium is attained in both "direct" and "reverse" experiments, this is true only of the benzene in the case of the solutions. The reason is quite clear, namely, the very slow movement of the slightly volatile iodine through the concentrated benzene vapour, an explanation in agreement with the observed slowness of diffusion of benzene vapour through air. Even in "reverse" experiments, where the iodine distils from one vessel at 100° into another at 25°, equilibrium is not attained in four days. The sorption of the iodine by the charcoal as shown in Table IV is reflected in the diminished relative volatility of the iodine when present in smaller amounts. It is possible also that both iodine and benzene in solution are subject to increase in sorption with time.

From the results in Table IV it appears that the sorption of benzene diminishes with increasing concentration of iodine, but in spite of numerical agreement between corresponding experiments (Tables III and IV) we are unable to explain why the sorption of benzene was constant (Table III) where the iodine was kept constant and the amount of charcoal was varied.

It is clear that in future experiments the temperature of the charcoal should be much lower, in order that results shall be obtained more directly comparable with those of ordinary, "relative" sorption experiments. In one "relative" measurement comparable with the last two experiments of Table IV, 10 c.c. of 0·4*N*-iodine were treated with 1·0714 grams of charcoal at 100° for eleven hours, and 0·0905 gram of iodine then remained in solution, as compared with the 0·05 gram distilling over in the other experiments.

It further follows that, even although the true sorption of benzene is quite comparable with that of iodine, the ordinary measurement of the relative sorption of iodine by charcoal is not appreciably in error, on account of the strong positive sorption here exhibited. It would be quite otherwise in such cases as aqueous solutions of electrolytes.

It is probable that a complete elucidation of the equilibria in this system could be obtained by adopting the device of initially placing various amounts of iodine in the upper bulb with the charcoal. The equilibria attained in such "semi-direct" experiments, with iodine solution or benzene in the lower bulb, could then

be checked by corresponding "reverse" experiments. In this manner the method might be applied to the cases of non-volatile solutes. The work was, however, broken off at this point in order to study the especially interesting case of acetic acid in toluene (Schmidt-Walter, *Kolloid Zeitsch.*, 1914, **14**, 242) where the relative sorption is actually reversed in concentrated solution.

Summary.

(1) A general method is described of determining the true amounts of sorption of solute and solvent to supplement the ordinary method, which yields relative values only. The error in the ordinary method is inappreciable except in concentrated solutions or where the solute does not exhibit strong positive sorption. In such cases both the proportionality constant and the exponent in the exponential formula are altered.

(2) Sorption of benzene from iodine solutions is less than that from pure solvent.

In conclusion, we wish to thank Professor J. W. McBain for the interest he has taken in our work.

The University of Bristol. [*Received, February 9th*, 1921.]

LVIII.—*On Interfacial Tension. Part I. The Statical Measurement of Interfacial Tension in Absolute Units.*

By William Colebrook Reynolds.

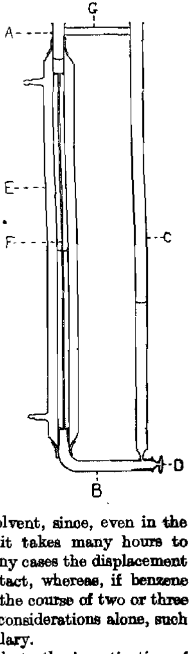
In January of last year the author exhibited at the Microscopical Symposium of the Faraday Society several emulsions which possessed the property of becoming inverted without alteration in composition when warmed, that is, the disperse phase became the continuous phase, and he demonstrated that several of the inverted emulsions could be completely reversed, that is, the original disperse phase could again become the disperse phase when the inverted emulsions were submitted to friction or lowered temperature. But, although many such emulsions, varying somewhat in composition, could be prepared, he was unable to give a satisfactory explanation of the nature of the phase changes, and as interfacial tension and

adsorption, and their change with temperature, appeared to offer the most likely explanation, the present investigation was undertaken.

Two methods have been employed to measure interfacial tension. (1) Quincke's Statical Method (*Ann. Phys. Chem.*, 1870, **139**, 1), which is based upon a consideration of the dimensions and shape of the drops of one liquid lying at rest in a surrounding, immiscible liquid. The experimental errors in the determination are somewhat high, especially in the case of mercury.

(2) The Dynamical Method (*Zeitsch. physikal. Chem.*, 1899, **31**, 42), which has been much used by Donnan and other workers. In this process the interfacial tension is calculated from a consideration of the forces operating on a drop of one liquid forming in a second immiscible liquid, at the moment that the drop is detached from a pipette, to the orifice of which a particular form has been given.

FIG. 1.



The author finds that a modification of the capillary method of measuring surface tension can be employed to measure interfacial tension, in dynes per cm., with great accuracy, providing certain simple precautions are taken. An essential condition is that the perfectly cleaned tube must be completely filled with the liquid which has the greater surface tension (in general, an aqueous solution), and the other immiscible liquid must travel continuously in one direction only. The measurements are completely falsified if the aqueous solution is allowed to advance along a surface that has been wetted by an immiscible organic solvent, since, even in the simplest cases, such as benzene–water, it takes many hours to displace the former completely, and in many cases the displacement is not complete after several weeks' contact, whereas, if benzene displaces water, equilibrium is reached in the course of two or three minutes, the time depending on viscosity considerations alone, such as the length and the diameter of the capillary.

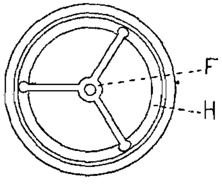
A convenient form of apparatus suitable to the investigation of all transparent solvents, is shown in sectional elevation in Fig. 1.

A simple modification adapted for measurements with opaque liquids, such as mercury, will be described in Part III.

A is a burette the graduation marks of which completely encircle the tube. This is surrounded by a water-jacket, *E*. *B* is a connecting tube of similar bore. *C* is a plain glass tube connecting with *B* through a glass cock, *D*. To prevent undue strain the wooden block, *G*, was fastened between *A* and *C*.

When the interfacial tension of colloidal sols is being measured, it is necessary to keep the tube under observation for several hours; the only form of cock that will withstand a head of liquid without any leakage whatever when absolutely free from all traces of lubricant (which must be entirely excluded) is the internally fitting cock used on calcium chloride tubes. If liquids lighter than water only are to be measured, *B* and *C* can be dispensed with, and a burette with a perfectly fitting tap, free from lubricant, will suffice.

FIG. 2.



The capillary tube, *F*, was maintained in a central position in the burette by three short glass rods fused on at either end perpendicularly to its length, and about 120° apart (Fig. 2). The length of these rods was adjusted by fusing the ends in a small flame, until the whole just fitted in the burette tube, where it rested on the glass collar, *H*, cut from a stout tube somewhat smaller than the burette. The diameter at both ends of the tube was measured by the microscopic method, and the uniformity of the bore was proved by the constant length of a thread of mercury when occupying different positions in the tube.

The capillary tube consisted of a machine-made tube, about 42 cm. long, of uniform circular bore throughout the whole length. The selection of the tube is of the greatest importance. Hand-drawn capillaries are very inferior, for in addition to the defect of their tapering bore, it is almost impossible to fracture them at right angles to their length, owing to the thinness of their walls, and the error in determining the bore by the microscopic method is considerable, the observed diameter almost always exceeding the actual diameter. The author believes that the use of hand-drawn capillaries accounts for the widely varying values recorded for the surface tension of water, and also that the experimental error in Quincke's statical method is probably far greater than that in either capillary or ripple observations. These discrepancies have given rise to the sugges-

tion that the surface tension of water measured by the dynamical method immediately after the surface is formed is different from that determined by the statical method. An accurate value was of great importance in the present investigation. It was found that London tap-water and distilled water free from ammonia had the same surface tension, in air and in a vacuum, and that the surface tension of water was the same, whether determined by Lord Rayleigh's dynamical "ripple" method (*Phil. Mag.*, 1890, [v], **30**, 386) or by the statical method, the mean values in dynes per cm. being 76·7/0°, 73·6/18°, 70·0/36°, 64·8/69°, and 60·9/89°.

Before the apparatus was used three corrections had to be determined. When a small tube is surrounded by a larger, the capillary rise, due to surface or interfacial tension in the smaller tube, is greater than the difference in height between the liquid surfaces, due to the capillary rise in the wider tube. Again, the reading of the height of the liquids in the tubes on the burette scale of c.c. had to be corrected to cm.; lastly, a correction had to be applied for the meniscus. The three corrections were simultaneously made as follows: the height of the capillary rise (h') of water in the smaller tube was determined in cm. when the latter was standing in an open vessel, the tube was then placed in the partly filled burette, and the rise (h'') noted in terms of the scale divisions, reading from the lower edge of the meniscus. In measurements of surface or interfacial tension in the apparatus, if h, in terms of scale divisions, is the difference in height of the liquids in the two tubes read from the lower edge of the meniscus, the true height in cm., corrected for the three points noted above, is given by $\frac{hh'}{h''}$.

To illustrate the use of the apparatus, one example, the case of benzene–water, is given. The whole apparatus was first filled with concentrated sulphuric acid saturated with potassium dichromate, and allowed to remain for at least half-an-hour; the mixture was then poured out and the apparatus repeatedly washed with water. The burette was filled with distilled water, water was admitted into the jacket at the desired temperature, and the tap was opened sufficiently to allow the level of the water to fall very slowly. As it fell benzene was poured in to maintain the level, and this process was continued until the benzene had entered the capillary. If the incoming liquid travels too quickly, and the displaced liquid in the capillary has not time to drain away from the walls, it may collect and form a bead, which breaks the column and necessitates a fresh start; this is particularly liable to occur when viscous liquids are being employed. The tap was then closed and readings were taken at intervals.

When pure benzene was employed, the position of equilibrium was reached in about three minutes. Commercially pure benzene contains an unascertained impurity, which causes adsorption at the interface, and for this reason the interfacial tension diminishes slowly for many hours. This impurity is readily removed when the benzene is shaken with a little fuming sulphuric acid for fifteen minutes, washed with diluted alkali and with water, and distilled.

The density of distilled water and of benzene at the temperature of the experiment was determined. The interfacial tension was calculated from the relation

$$T = \frac{dghh'(D' - D'')}{4h''}$$

where T = the interfacial tension, d the diameter of the tube (0·0614 cm.), D' the density of the water, D'' the density of the benzene, and $g = 981$.

The expression $\frac{dh'g}{4h''}$ is a constant for the apparatus, its value here being 15·63. Hence $T = h(D' - D'') \times 15{\cdot}63$ dynes per cm.

When liquids heavier than water were being examined, the liquid was introduced into the empty tube, C, and allowed to enter the lower portion of the burette, which was already partly filled with the aqueous solution. The liquid was allowed to rise until it was observed to enter the lower end of the capillary, the cock was then closed, and the measurements were made in the manner described above.

The interfacial tensions of a number of immiscible solvents and aqueous solutions are recorded in Part II. of this investigation (this vol., p. 466).

A comparison of interfacial tensions determined by this process and by the dynamical drop method is of interest. In the table below, in column II., the interfacial tensions of six solvents in contact with water, determined by the statical method, are recorded, and in column III. the values found by the dynamical method. In the latter measurements the liquids were never allowed to leave the pipette at a rate exceeding 1 c.c. per minute.*

* Except in the case of benzene, the more slowly the drops form the large they grow when water is the immiscible liquid; carbon tetrachloride, however, is only slightly affected. With colloidal sols, on the other hand, the interfacial tension diminishes as the surface increases in age, and the size of the drops is smaller the more slowly they are allowed to form. Very dilute solutions of salts, acids, and bases behave like water, but concentrated solutions simulate colloidal sols, that is, they behave as if they contained molecular complexes comparable with those in colloidal sols, showing adsorption and surface concentration.

The ratio of the statical to the dynamical interfacial tension is recorded in column IV. From the mean ratio it would appear that interfacial tension, measured by the dynamical method and calculated as below, would, when multiplied by the factor 1·26, give very approximately the true interfacial tension.

I	II	III	IV
Ethyl ether	10·6	7·7	1·39
Amyl alcohol	4·8	3·8	1·26
Benzene	34·4	28·0	1·23
Nitrobenzene	24·7	21·0	1·18
Chloroform	33·3	26·7	1·25
Carbon tetrachloride	43·8	34·1	1·29

The dynamical results were calculated on the assumption that

$$T = \frac{981 V(D' - D'')}{n\pi d} \text{ dynes per cm.,}$$

where V = the volume of the pipette, n = the number of drops, and d = the diameter of the orifice.

This calculation and that for the determination of the surface tension of liquids by an analogous method have been the subject of several investigations, particularly by Guye and Perrot, and by Kohlrausch and Lohstein (*vide* Lewis, *Phil. Mag.*, 1908, [vi], **15**, 449).

Undoubtedly the principal source of error in this calculation arises from the assumption that the perimeter of the section of rupture is identical with the circumference of the orifice of the pipette. Darling, in his "Liquid Drops and Globules," has proved conclusively that constriction occurs previous to separation, and this was deduced by Vaillant (*Compt. rend.*, 1914. **158**, 936). The behaviour of the liquid column resembles that of a steel rod in a testing machine, and into the equation a term should be introduced involving viscosity, as this, in addition to surface tension, tends to prevent disengagement of the drops.

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[*Received, February 10th*, 1921.]

LIX.—*On Interfacial Tension. Part II. The Relation between Interfacial and Surface Tension in Sundry Organic Solvents in Contact with Aqueous Solutions.*

By WILLIAM COLEBROOK REYNOLDS.

IN Part I of this communication the author has described an apparatus in which interfacial tension can be measured in absolute units. It is now proved that there is a very intimate connexion between the interfacial tension at the surface separating immiscible liquids and the surface tensions of the liquids.

From a consideration of the conception that surface tension is due to the attraction of molecules lying in the surface by those immediately surrounding and beneath them, it appeared probable that if the internal forces giving rise to this phenomenon were, like gravitational or electrostatic force, independent of the chemical nature of the molecules concerned, interfacial tension would be the difference between the two surface tensions.

This hypothesis, when tested, was found to be only very approximately true in some cases, whilst in others the discrepancy was considerable. Further investigation revealed the cause.

When two liquids are in contact, each is saturated with the other at the surface of contact, consequently it is necessary to substitute for the surface tensions of the two liquids those of their mutually saturated solutions. When the latter were determined, with the precautions detailed below, it was found that the following law was accurately true in the case of pure solvents:—The interfacial tension between two liquids A and B is the difference between the surface tension of A saturated with B and the surface tension of B saturated with A.

When the interfacial tension is measured by the capillary method described in Part I, due consideration must be given to the phenomena of wetting. All the liquids described in this paper wet glass; here, the capillary rise is the difference. In Part III, where mercury, which does not wet glass, is dealt with, the capillary forces act in the same direction in glass tubes; hence the capillary depression is the sum. A convention as to the sign of the forces has thus to be adopted, since the true interfacial tension is always the difference between the forces.

The following appear to form exceptions to the law:

(1) Immiscible liquids that react chemically.

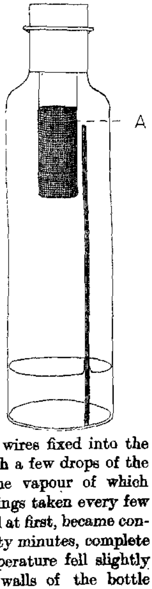
(2) Mercury and liquid amalgams in contact with certain electrolytes.

(3) The old interface separating certain solutions where surface concentration has occurred.

The Measurement of the Surface Tension of Saturated Liquids.

When the surface tensions of mutually saturated liquids were being measured, the liquids were shaken in a separator and run into cylindrical bottles, about 4½ cm. in diameter, with straight sides about 12½ cm. in height. Selected capillary tubes were employed (see Part I), the same tubes being used for all the measurements recorded. The capillary tube was allowed to rest in a vertical position against the walls of the bottle (see Fig. 1). The bottle and the capillary tube were cleaned (see Part I) and dried in an air-oven before each measurement. When observations were being made, the bottle was inclined to allow the liquid to fill the tube completely, and the position of equilibrium of the column on falling was noted. The bottle stood in a water-bath at a known temperature, except at the moment when measurements were being taken, and was closed by a cork to prevent evaporation of volatile, saturating liquid. It was found, however, that there was a considerable error in such determinations due to volatilisation of the saturating liquid into the space above the liquid, whereby the surface layer became weaker, and in the case of aqueous solutions the observed tensions were too high. This source of error was eliminated by a simple expedient (Fig. 1). This consisted of a cylinder of wire gauze (A) supported by two wires fixed into the cork and filled with cotton wool moistened with a few drops of the saturating liquid (chloroform, ether, etc.), the vapour of which maintained saturation of the air space. Readings taken every few minutes proved that the capillary rise, which fell at first, became constant after a short interval, usually thirty to forty minutes, complete saturation having been effected. If the temperature fell slightly subsequently, condensation occurred on the walls of the bottle and an oily layer appeared, but the position of equilibrium remained constant.

FIG. 1.



It was subsequently found that in the case of pure liquids the shaking in a separator was unnecessary, since only the surfaces

were active. Exactly the same effect was obtained when a pure solvent was placed in the bottle and the air space was saturated with the vapour of the immiscible liquid, as when the two liquids had been previously shaken together. This circumstance made it possible to take measurements when dealing with certain colloidal sols such as gelatin, where almost permanent emulsification occurred on shaking the sol with an immiscible liquid.

In Table I, the interfacial tension of the liquid mentioned in column 1 in contact with water is given in column 6. The liquids were purified and redistilled. The difference between the values in columns 2 and 4 is given in column 5. The close agreement between the calculated values in column 5 and the observed values in column 6 will be noted. Column 7 gives the temperature at which the observations were made.

TABLE I.

Oil.	Surface tension of water saturated with the oil.	Surface tension of the dry oil.	Surface tension of the oil saturated with water.	Interfacial tension calculated.	Interfacial tension observed.	Temperature.
Benzene	63·2	28·4	28·8	34·4	34·4	19°
Ethyl ether	28·1	17·7	17·5	10·6	10·6	18
Aniline	46·4	41·9	42·2	4·2	4·8	26
Chloroform	59·8	27·2	26·4	33·4	33·3	18
Carbon tetrachloride	70·2	26·7	26·7	43·5	43·8	17
Nitrobenzene	67·9	43·4	43·2	24·7	24·7	18

The interfacial tension of pure liquids is invariable at constant temperature; surfaces had the same tension after five minutes and after twenty-four hours in each of the above cases. When, however, one of the liquids is complex, that is, an aqueous solution, colloidal sol, or mixture of two or more organic solvents, the interfacial tension frequently depends on the age of the contact surface, because concentration of one or more of the constituents of the solutions often occurs. It seems probable that the law stated above holds true in nearly all phases of these cases also, but where the value of the tension is rapidly changing it is only practicable to make comparable observations of the interfacial and surface tensions in particular circumstances, and at times dynamical methods must be employed where statical ones are unsuitable. The author has endeavoured to find in each case the interfacial tension of freshly formed surfaces, and of old surfaces when final equilibrium had been reached. In all these complex contact surfaces so far examined, *the underlying cause of surface concentration appears to be this:* at any given temperature the interfacial tension tends towards a minimum; it never increases spontaneously with age. If, therefore, one of the constituents of a mixture has a lower interfacial tension

than the others, it is attracted towards the contact surface, the movement in the case of organic solvents and of many colloidal sols proceeding for many hours. The three classes are considered separately below.

Mixed Organic Solvents.

The figures in Table II prove that the law holds good in the case of mixtures of organic solvents when the interfaces are freshly formed or old surfaces are disturbed. In some cases mixtures of nearly allied solvents behave like pure solvents, and the interfacial tension retains the same value in the case of old surfaces. Where, however, one of the ingredients has a much lower interfacial tension than the other constituents, this is found to be slowly drawn towards the surface of separation, concentration proceeding here for many hours, during which the interfacial tension falls slowly. Thus, when water is brought into contact with benzene to which a small proportion of a liquid (such as oleic acid) which has a lower interfacial tension than itself has been added, the interfacial tension falls slowly for several hours. The question arises, Does the interfacial law still hold in the cases of the older surfaces when equilibrium has been reached and the interfacial tension has become constant? It appears that the apparent equilibrium applies only to the contact surface. The oleic acid in twenty-four hours reaches a new concentration and the water a new degree of saturation at the interface, but the changes do not extend to the body of the two liquids, which retain the same surface tensions as they had when the contact surfaces were fresh. This class therefore does not obey the law in regard to old surfaces, though this may in reality be due to our inability to measure the surface tensions at the actual interface.

All the various commercial products from petroleum, even after they had been distilled with steam in the presence of sodium hydroxide to remove traces of saponifiable oils, showed more or less adsorption with time, due to the presence of constituents of low interfacial tension.

In Table II, the values of the tensions for the mixed solvents shown in column I are given. Where two figures are bracketed, the larger refers to surfaces five minutes old, and the smaller to those twenty-four hours old. Where only one figure is given, this applies to both.

In several instances surface concentration had already occurred to a measurable extent at surfaces five minutes old, and the interfacial tension, even at this early stage, was already somewhat below the calculated value. In the case of liquid paraffin, B.P., the adsorption was so rapid that no accurate measurement of the

TABLE II.

Oil.	Surface tension of water saturated with the oil.	Surface tension of the oil.	Surface tension of the oil saturated with water.	Interfacial tension, calculated.	Interfacial tension, observed.	Temperature.
Amyl alcohol	26·3	24·4	21·5	4·8	4·8	18°
Cresylic acid	37·8	37·1	34·3	3·5	3·9	18
Petrol	69·6	22·0	22·0	47·6	{46·4, 37·1}	18
White spirit	69·5	25·2	25·1	44·4	{42·3, 39·4}	18
Paraffin oil	73·0	24·8	24·7	48·3	{48·7, 43·1}	18
Liquid Paraffin, B.P.......	73·0	31·6	31·5	41·5	{(41), 15·1}	17
Turpentine	63·0	27·2	27·2	35·8	{34·2, 28·8}	18
Amyl alcohol, 5 % + Benzene, 95 % ...	41·4	28·0	26·0	15·4	{16·7, 16·1}	17
Aniline, 5 % + Benzene, 95 %	57·1	29·4	29·6	27·5	27·1	17
Cresylic acid, 1 % + Benzene, 99 % ...	56·5	29·1	28·7	27·8	27·5	17
Oleic acid, 1 % + Benzene, 99 %	63·0	29·3	29·2	34·8	{30·8, 24·2}	17

fresh surface was possible by the author's statical method. By the dynamical method the value 41 was obtained when drops were allowed to form rapidly from a special pipette of wide bore. When the drops formed slowly the value fell to about one-half.

Aqueous Solutions.

In Table III the interfacial tensions between benzene and aqueous solutions of the compounds in column 1 are recorded. The differences between the values in columns 5 and 6 are given in column 7; they are in close agreement with the observed values in column 8.

TABLE III.

Solute.	Density of the aqueous solution.	Gram-mols. of solute per litre.	Surface tension of solution.	Surface tension of solution saturated with benzene.	Surface tension of benzene saturated with the solution.	Interfacial tension, calculated.	Interfacial tension, observed.	Temperature.
Sodium chloride ...	1·0012	0·1	72·2	64·0	28·9	35·1	34·9	18°
,, ,, ...	1·041	1·0	74·4	65·5	28·7	36·8	37·3	19·5
,, ,, ...	1·187	5·0	83·5	72·0	29·1	42·9	42·5	17
Sodium hydroxide ...	1·046	1·0	74·8	65·3	28·9	36·4	37·7	18
,, ,, ...	1·191	5·0	84·5	72·7	29·0	43·7	44·7	17
Sulphuric acid	1·0275	0·5	73·0	62·5	28·0	34·5	35·0	25
,, ,, ...	1·151	2·5	75·6	65·7	28·9	36·8	36·6	18
,, ,, ...	1·291	5·0	77·45	66·2	28·9	37·3	37·1	18
Sodium thiosulphate	1·041	0·1	73·5	63·4	28·7	34·7	34·6	20
Glycerol	1·114	5·0	70·9	57·7	28·7	29·0	28·6	20
Sucrose	1·014	0·1	73·7	62·7	28·7	34·0	34·4	20
,, ...	1·135	1·0	75·3	63·0	28·9	34·1	34·1	18

The law holds true in all these cases, the interfacial tension after five minutes remaining constant for twenty-four hours. This does not mean that surface concentration does not take place, but it does prove that if it occurs it is complete, within measurable limits, in the case of surfaces five minutes old.

Colloidal Sols.

The sols were prepared as follows and kept under sterile conditions.

Gelatin.—Coignets Extra (Gold Label) was filtered. The viscosity of this sol varies considerably with its age, but the interfacial tension was found to be independent of the viscosity.

Gum Acacia.—Filtered aqueous sol.

Gum Tragacanth.—The powdered gum, moistened with a little alcohol, was treated with water, concentrated on the water-bath to remove the alcohol, diluted to volume and filtered under sterile conditions in an incubator at 37°. The insoluble matter adsorbed much of the gum, the original 0·5 per cent. sol only containing 0·32 per cent. after filtration.

Starch.—Two per cent. unfiltered sols of various starches differ greatly in viscosity, that of potato starch being 53·2 (water = 1), and that of rice starch only 3·7.

The sterile sols were allowed to stand in tall, covered cylinders for some days while the insoluble matter slowly settled at an average rate of about 2 cm. per day. The insoluble matter adsorbed a large proportion of the starch, the decanted clear arrowroot sol only leaving 0·488 per cent. on evaporation instead of 2 per cent.; the viscosity meanwhile had fallen from 7·6 (unfiltered) to 1·52 (clear, decanted).

Lord Rayleigh's classical experiments (*Proc. Roy. Soc.*, 1890, **47**, 281) have proved that the surface tension of soap solutions, when the surface is not more than one-hundredth of a second old, is the same as that of water, although when the surface is only a few seconds old the value may fall to approximately one-half, owing to the extremely rapid concentration of the soap at the surface. If colloidal sols behave like soap solutions and have the same surface tension as water in freshly formed surfaces, it might be anticipated that the sols in contact with benzene would, at the moment of contact, have the same interfacial tension as benzene and water. The application of ripple and jet methods of measurement to the sols mentioned below does not appear to have been undertaken. By Donnan's drop-pipette method it is possible to make a comparison of the interfacial tension between benzene and colloidal sols with that between benzene and water, and if the drops are forming

very rapidly (about ninety per minute) the surfaces are still fairly fresh.

In Table IV the number of drops of benzene formed in the sols is compared with the corresponding number formed in water at the same rate at 18°. From these numbers it appears that surface concentration in these cases does not take place so rapidly as in soap solutions, where very much larger drop numbers are obtained under the same conditions, and that the sols in question have nearly the same interfacial tension at this stage as water.

TABLE IV.

Sol.	Number of drops of benzene formed.	Interfacial tension observed after 15 minutes.
[Water	84	34·4]
0·5 per cent. Gelatin	96	21·0
0·1 ,, ,, ,,	85	26·1
10 ,, ,, Acacia	87	32·9
5 ,, ,, ,,	86	34·6
1 ,, ,, ,,	85	36·3
0·5 ,, ,, Tragacanth, 0·32 *	92	25·9
2 ,, ,, Arrowroot, 0·488*	85	36·3
2 ,, ,, Patent Starch	85	36·3

* Percentage concentration after clarification.

The interfacial tension of these sols in contact with benzene, measured by the statical method when the surfaces were fifteen minutes old, is recorded in column 3. From a comparison with the drop numbers in column 2 it will be seen that considerable concentration had occurred in the case of gelatin and tragacanth. As the interface grew older equilibrium generally supervened very slowly, owing to the lowering of the surface tension as surface concentration of the colloid proceeded. It was therefore necessary to make observations at intervals over twenty-four hours; even then it was doubtful in a few cases whether adsorption had reached measurable limits, but it was difficult to keep the apparatus at a constant temperature for longer periods by means of the water-jacket, and the error due to the variation in temperature effected minute changes in the interfacial tension. Starch sols formed an exception, for here equilibrium was reached almost immediately. But it was not only the interfacial tension of the sols in contact with benzene that changed with time. The surface tensions of the sols, alone and also when saturated with benzene, also altered, and it was found that the values of these tensions, observed at surfaces of the same age, were in agreement with the interfacial law.

The general behaviour will be made evident by considering one example in detail. A 10 per cent. sol of gum acacia had a surface

tension of 72·8 dynes per cm. when the surface was freshly disturbed, but the value diminished gradually for several hours as surface concentration occurred, and after twenty-four hours it was 69·0. The surface tension of this sol saturated with benzene changed similarly, and was found to be 53·0 after twenty-four hours. The interfacial tension in contact with benzene was 32·9 dynes per cm. when the contact surfaces were fifteen minutes old, but fell to 27·6 after three hours, and to 25·9 after twenty-four hours.

In Table V are given the results obtained with surfaces twenty-four hours old. Where two values are bracketed the higher refers to the fresh surface, and the lower to the twenty-four hour-old surface; otherwise, the value does not alter with age. The difference between the values in columns 3 and 4 is given in column 5, and agrees fairly well with the figure in column 6, although the agreement is not so good as that in *Table III*.

TABLE V.

Sol.	Surface tension of the sol.	Surface tension, after 24 hours, of the sol saturated with benzene.	Surface tension of benzene saturated with sol.	Interfacial tension after 24 hours, calculated.	Interfacial tension observed after 24 hours.	Temperature.
0·5 per cent. Gelatin	{71·1, 65·5}	48·2	28·9	19·3	19·9	18°
0·1 ,, ,, ,,	{69·4, 66·4}	50·2	29·0	21·2	23·4	17
10 ,, ,, Gum Acacia	{72·8, 69·0}	53·0	28·0	24·1	25·9	18
5 ,, ,, ,, ,,	{73·0, 70·3}	56·0	28·7	27·3	29·9	19
1 ,, ,, ,, ,,	73·5	62·9	28·9	34·0	34·5	18
0·5 ,, ,, Gum Tragacanth, 0·32*	{70·0, 57·8}	45·3	28·9	16·4	19·2	18
2 ,, ,, Arrowroot, 0·488*	73	64·0	28·8	35·2	35·7	19
2 ,, ,, Patent Starch	73·8	63·5	28·9	34·6	36·3	18

* Percentage concentration after clarification.

The meniscus of a twenty-four hour-old sol in a capillary tube standing in a closed bottle exhibits in some cases a distinctly gel-like character. When the contents of the tube are allowed to exude slowly on to a watch glass, this gel-like surface, retaining the form of the meniscus, and having a depth equal to its diameter, may be seen floating in the body of the sol for some minutes before it is absorbed.

Soap Sols.

The surface and interfacial tensions of nine dilutions of soap sols, belonging to three typical classes, in contact with benzene were investigated. The behaviour of these sols resembled in general

that of the colloid sols mentioned above, the chief difference being the more rapid surface concentration in the case of the soap sols.

From Lord Rayleigh's observations on surface tension (*loc. cit.*) it may be anticipated that the interfacial tension between the soap sols and benzene, at the moment of contact, would be the same as that between water and benzene. The freshest contacts that the author observed were those formed in the manner described in the case of the colloid sols.

In column 8 of Table VI the number of drops of benzene, formed in the soap sols as quickly as they could be accurately counted is compared with the number of drops formed in water in the same circumstances. The results prove that the interfacial tensions at these contact surfaces, which must be considerably under one second old, are 75—21 per cent. of that of benzene–water contacts (34·4 dynes per cm.).

The interfacial tension determined by the preceding statical method became constant after five minutes in seven out of the nine dilutions, whilst, in the surface tension measurements of the sols themselves, in contact with air, equilibrium was only established after 10—120 minutes. Surface concentration therefore appears to be more rapid at benzene- than at air-contacts.

It is probable that very fresh contacts, one-hundredth of a second old, would obey the interfacial law stated above. Old contacts, when surface concentration was complete, did not do so, the observed interfacial tension being higher than that calculated from the surface tensions of the immiscible liquids. This may be due to a smaller surface concentration at benzene contacts than at saturated soap sol-air surfaces, but the measurements may be appreciably affected by hydrolysis of the soap, the free fatty acid being dissolved by the benzene and a more alkaline, aqueous sol remaining.

The soap sols were prepared as follows. Ten grams of the oil mentioned in column 1 (Table VI) were saponified by that volume of a solution of sodium hydroxide (D 1·30) which experience had shown yielded a neutral soap, the soap was dissolved and the solution made up to 100 c.c. The other dilutions were prepared from the 10 per cent. sol. A 10 per cent. cocoa-nut sol crystallised after some days, and a 1 per cent. sol gelled, but on warming and cooling both remained clear mobile fluids for more than twenty-four hours, and the measurements were made on the recently cooled sols. All observations were made at 17—18°. The observed interfacial tensions for contacts after twenty-four hours and after five minutes are given in columns 6 and 7 respectively; the calculated tensions, that is the difference of the values in columns 3 and 4, are given in column 5.

TABLE VI.

Soap sol.	Surface tension of the sol after 4 hours.	Surface tension of the sol saturated with benzene, after 24 hours.	Surface tension of benzene saturated with the sol.	Interfacial tension calculated.	Interfacial tension observed after 24 hours.	Interfacial tension observed after 5 minutes.	Number of drops of benzene.
{Water	73·4	63·2	28·6	34·6	34·4	34·4	84]
10 % Castor Oil	35·1	30·9	28·6	2·3	3·0	3·0	398
1 % ,, ,, ...	35·8	32·0	28·6	3·4	5·6	5·7	249
0·1 % ,, ,, ...	43·5	46·2	28·6	17·6	23·2	23·2	124
10 % Olein (commercial) ...	26·6	26·3	28·6	−2·3	1·6	1·6	237
1 % ,, ,, ...	25·7	26·8	28·6	−1·8	3·3	3·5	214
0·1 % ,, ,, ...	25·4	38·1	28·6	9·5	17·2	21·3	113
10 % Cocoanut Oil (pressed)	26·5	26·7	28·6	−1·9	2·7	2·7	306
1 % ,, ,, ,,	23·3	27·7	28·6	−0·9	5·2	5·2	249
0·1 % ,, ,, ,,	29·4	50·7	28·6	22·1	27·6	27·6	114

The author's results indicate that surface concentration is much more widely prevalent than is generally supposed, and that it affects solutions of every description. It seems not improbable that this phenomenon affects certain physical measurements such as viscosity and lubrication tests.

The study of interfacial tension may throw light upon many chemical and biological problems. Whenever investigation proves that the interfacial tension of two immiscible liquids is not constant at a given temperature, or that the liquids do not obey the interfacial tension law, surface concentration, or electrical or chemical action, is indicated.

In Part III it will be shown that interesting electro-chemical relationships can be explained by means of the interfacial tension law.

Two minor instances of its use in directing attention to chemical changes were noted during the investigation, and are perhaps worth recording.

Carbon disulphide in contact with water and air does not obey the interfacial tension law. The surface tension of water saturated with carbon disulphide is 72·2, and that of carbon disulphide saturated with water is 32·1; the interfacial tension should therefore be the difference, 40·1. The observed figure was 49·3.

The discrepancy was found to be due to the chemical interaction of air, water, and carbon disulphide. When the two liquids are shaken together in a separator for a few seconds, an almost invisible film of a substance insoluble in either liquid separates at the interface. This is made more apparent by draining off the carbon disulphide, when the film is compressed into the restricted area just above the tap and is thus more easily seen. When the two

liquids are allowed to remain in contact for several hours in a wide, stoppered bottle, decomposition proceeds, and a yellowish-brown precipitate forms at the interface. Purification of the carbon disulphide in various ways failed to yield a product which did not show these changes, and samples obtained from three firms behaved alike. The nature of the oxidation product was not investigated.

Turpentine in contact with air undergoes oxidation so rapidly that the accurate measurement of its interfacial tension in contact with water is made very difficult. The slightest contact with air during distillation makes a great difference in the product. Samples of the same specimen of turpentine were distilled as described in column 1 below. The interfacial tension of the distillate in contact with water is noted in column 2.

Distilled in a vacuum with an air-inlet tube passing to the bottom of the flask	10·3
Distilled at the ordinary pressure from a half-filled flask	25·8
Steam distilled from a half-filled flask	27·8
Distilled and cooled in a vacuum	34·2

All these distillates had the same surface tension in contact with air, namely, 27·2. They changed slowly in character when stored in partly filled, stoppered bottles. Thus the sample with an interfacial tension 25·8 gave the value 20·9 after a few hours, and after it had been stored for sixteen days in a half-filled bottle the interfacial tension had fallen to 12·9. The specimen which originally showed 34·2, after having been kept for 111 days in a nearly full bottle, gave the value 20·1, and another portion of the same specimen, after 111 days' storage in a bottle, the neck of which was plugged with cotton wool, had an interfacial tension of 1·06 only. The changed products, after having been shaken with a dilute solution of sodium hydroxide to remove acid matter which had been formed, and redistilled in a vacuum, regained their original properties; it was thus shown that the oxidation only affected a moderate proportion of the whole liquid.

The change of interfacial tension with temperature will be the subject of a further communication.

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[*Received, February 10th, 1921.*]

LX.—*Chlorine Overvoltages.*

By EDGAR NEWBERY.

IN a series of papers (T., 1916, **109**, 1051 *et seq.*) the author has given an account of the overvoltages of a number of electrodes during the liberation of hydrogen, oxygen, or metal, and has suggested a theory to account for the results obtained.

With the view of further testing this theory and, if possible, extending its scope, it was considered advisable to determine the over-voltage of as many electrodes as possible during liberation of chlorine; it was felt that although, owing to the great chemical activity of chlorine, very few electrodes were available, yet when treated as supplementary to the larger work already done, the knowledge to be gained thereby would prove of value both from a theoretical and a practical point of view.

To avoid misunderstanding, the chlorine overvoltage of an electrode may be defined as the excess of the back electromotive force of that electrode above that of a standard chlorine electrode in the same electrolyte.*

EXPERIMENTAL.

The apparatus used was almost identical with that employed in previous work (T., 1914, **105**, 2420), the only important change being the employment of a very fine vernier potentiometer (made by H. Tinsley & Co., London) in place of the ordinary slide wire instrument. By means of two rheostats this was adjusted to read volts directly and the trouble of conversion avoided.

Temperature not being an important factor, a thermostat was not necessary. Generally it was $16° \pm 1°$. In all attempts made up to the present to determine the effect of temperature on overvoltage, other larger effects have so masked the temperature effect that no definite conclusions have been reached other than its

* This is unfortunately necessary owing to the fact that attempts are still being made, especially in America, to measure overvoltage without cutting off the charging current. Under these conditions the excess of the potential due to transfer resistance, resistance of electrolyte, etc., may be, and usually is, so great as completely to mask the true overvoltage. These secondary effects may be altered at will by changing the size of the electrodes, their distance apart, the position of the standard electrode, the shape of the electrode vessel, etc. Measurements taken under such conditions are almost meaningless, and conclusions based upon them correspondingly valueless. Illustrations of the effect of omitting to cut off the current have been given by the author (T., 1914, **105**, 2422), where it has been shown that errors of more than *1000* per cent. may be produced.

relative unimportance. Further work on this subject is, however, desirable, and will be attempted shortly.

The standard electrode used for the sake of convenience was in all cases the normal calomel electrode. In order to determine the exact relation between this electrode and the chlorine electrode without any assumptions as to boundary potential, etc., the following cell was made up :—

$$(Pt)Cl_2,N\text{-}HCl \mid N\text{-}HCl \mid N\text{-}KCl,Hg_2Cl_2,Hg.$$

Pure electrolytic chlorine was passed round a platinised glass electrode to form the chlorine electrode, and the electromotive force of the cell rose from 1·0460 volts to 1·0530 volts in half an hour and then remained constant within 0·5 millivolt for two hours, the temperature being 16°.

The following electrodes were examined: Copper, silver, gold, zinc, cadmium, mercury, aluminium, thallium, carbon (gas carbon and Acheson graphite), tin, lead, antimony, tantalum, bismuth, chromium, molybdenum, tungsten, manganese, iron, nickel, cobalt, rhodium, palladium, iridium, platinum.

Of these electrodes, only carbon, rhodium, iridium, and platinum are unattacked by anodic chlorine. Gold, chromium, palladium, and sometimes thallium show well-marked passivity phenomena; antimony, tantalum, tungsten, and sometimes thallium show valve action; copper, silver, mercury, and lead are slowly covered with a thick insulating coating; the remainder dissolve freely. The surface area of each electrode was approximately 1 sq. cm.

The following tables are compiled in the same manner as those given in previous communications, column *A* showing values obtained on first passing the current with an unused electrode, and column *B* the average of several sets of subsequent readings with the same electrode.

The electrolyte (unless otherwise stated) was *N*-hydrochloric acid. and the cathode a platinum plate.

Unattacked Electrodes.

Current in milli-amperes.	Carbon 1. A.	Carbon 1. B.	Carbon 2*. A.	Carbon 2*. B.	Graphite 1. A.	Graphite 1. B.	Graphite 2.* A.	Graphite 2.* B.
2	− 0·25	+ 0·12	0·15	0·32	0·05	0·02	0·19	0·19
4	− 0·20	0·16	0·22	0·38	0·09	0·03	0·40	0·24
6	− 0·15	0·20	0·45	0·40	0·11	0·03	0·43	0·28
10	− 0·10	0·25	0·46	0·42	0·12	0·04	0·44	0·34
20	0·00	0·32	0·46	0·46	0·15	0·09	0·43	0·40
50	+ 0·02	0·41	0·43	0·46	0·19	0·15	0·43	0·60
100	0·05	0·42	0·41	0·46	0·21	0·19	0·43	0·67
200	0·08	0·52	0·36	0·43	0·22	0·20	0·44	0·71
400	0·41	0·54	0·32	0·35	0·23	0·31	0·57	0·70
1000	0·41	0·53	0·27	0·30	0·30	0·32	0·65	0·70

* Coated with paraffin wax.

Current in milli-amperes.	Rhodium. A.	Rhodium. B.	Iridium. A.	Iridium. B.	Platinum. A.	Platinum. B.	Platinum in KCl. A.	Platinum in KCl. B.
2	0·00	0·08	0·02	0·14	− 0·03	0·00	0·04	0·38
4	0·00	0·09	0·03	0·15	0·00	0·00	0·05	0·40
6	0·01	0·10	0·05	0·15	0·00	0·00	0·05	0·42
10	0·03	0·12	0·06	0·16	0·00	0·02	0·06	0·44
20	0·05	0·14	0·07	0·17	0·01	0·18	0·09	0·44
50	0·15	0·15	0·17	0·18	0·02	0·18	0·26	0·45
100	0·23	0·17	0·21	0·19	0·04	0·18	0·34	0·45
200	0·27	0·22	0·23	0·19	0·45	0·18	0·40	0·46
400	0·29	0·29	0·20	0·19	0·46	0·15	0·40	0·46
1000	0·26	0·26	0·17	0·18	0·45	0·13	0·40	0·45

Passive Electrodes.

Current in milli-amperes.	Gold. A.	Gold. B.	Thallium. A.	Thallium. B.	Chromium. A.	Chromium. B.	Palladium. A.	Palladium. B.
2	− 0·26	− 0·26	< − 1·0	0·00	− 0·09	− 0·09	< − 0·5	< − 0·5
4	− 0·25	− 0·25	,,	0·05	− 0·10	− 0·10	,,	,,
6	− 0·24	− 0·25	,,	0·08	− 0·11	− 0·11	,,	,,
10	− 0·24	+ 0·21	,,	0·10	− 0·13	− 0·13	,,	,,
20	− 0·23	0·24	,,	0·13	− 0·14	− 0·14	,,	,,
50	− 0·22	0·28	+ 0·21	0·28	− 0·16	− 0·16	− 0·50	− 0·50
100	− 0·21	0·30	0·23	0·28	− 0·18	− 0·18	+ 0·06	+ 0·05
200	+ 0·30	0·30	0·21	0·21	− 0·19	− 0·19	0·07	0·06
400	0·28	0·28	0·12	0·08	− 0·20	− 0·20	0·06	0·07
1000	0·26	0·26	0·00	0·00	− 0·21	− 0·21	0·06	0·06

Effect of Time.

It has been pointed out in previous communications that it is a matter of considerable difficulty to distinguish between the effects of time and of current density. If, however, the general theory is borne in mind, it not only becomes easier to make this distinction but also the necessity for doing so appears of less importance.

Under certain fixed conditions of current density, nature of surface, etc., the electrode surface first becomes saturated with gas, and if no compound is formed, the single potential after the main current has been cut off is that of a normal gas electrode, and the overvoltage is therefore zero. If the current density is sufficiently great, one at least of the overvoltage compounds will tend to form under the influence of the great internal pressures set up in the electrode, and this compound will gradually form a saturated solid solution with the electrode surface.

The time taken to form this saturated solution will depend on the solubility of the compound, rate of formation, current density, etc., and will therefore vary greatly with different electrodes and under different conditions. When the saturated solution is formed, the single potential of the electrode is completely determined by the ionisation of the overvoltage compound, and the measured overvoltage then becomes constant. It is evident that the occurrence of an ideal condition of this type may be somewhat rare and

its attainment frequently very difficult, since the overvoltage may tend to rise owing to the formation of new compounds, or to fall owing to the break up of the electrode surface releasing the high pressures and allowing the compounds already present to decompose. It is therefore only by careful study of the figures given, in the light of this theory, that a true estimate of the single potentials of the overvoltage compounds can be made. In the preceding tables the time interval between readings in column *A* may be taken as approximately one minute. The values shown there should be compared with those given in the following tables.

Time Experiments.—These experiments were carried out exactly as those previously described (T., 1916, **109**, 1055), the electrodes being cleaned with fine emery cloth before each series of readings was made.

Gas Carbon 1.

Current in milli-amperes.	Time in minutes. 1.	2.	3.	4.	5.	10.	15.	20.	25.	30.
1	−0·26	−0·24	−0·22	−0·21	−0·20	−0·16	−0·14	−0·12	−0·10	−0·08
10	−0·01	0·00	0·00	+0·01	0·01	0·02	0·02	0·02	0·03	0·03
100	0·17	0·24	0·31	0·38	0·42	0·47	0·48	0·47	0·46	0·46
1000	0·44	0·45	0·46	0·46	0·46	0·46	0·46	0·46	0·47	0·47

Graphite I.

1	0·05	0·06	0·06	0·07	0·08	0·08	0·09	0·10	0·11	0·11
10	0·14	0·16	0·17	0·18	0·18	0·18	0·18	0·18	0·18	0·18
100	0·18	0·18	0·18	0·18	0·18	0·19	0·19	0·19	0·19	0·19
1000	0·24	0·25	0·25	0·26	0·28	0·34	0·36	0·40	0·42	0·45*

* Remained constant at 0·45 volt for a further 30 minutes.

Rhodium.

1	0·01	0·01	0·02	0·02	0·03	0·04	0·04	0·05	0·05	0·05
10	0·08	0·09	0·10	0·10	0·11	0·11	0·12	0·12	0·12	0·13
100	0·23	0·23	0·23	0·23	0·23	0·23	0·23	0·23	0·23	0·23
1000	0·27	0·28	0·29	0·29	0·29	0·29	0·28	0·28	0·28	0·28

Iridium.

1	0·08	0·10	0·11	0·11	0·11	0·12	0·12	0·12	0·12	0·13
10	0·13	0·13	0·14	0·14	0·14	0·14	0·14	0·14	0·15	0·15
100	0·16	0·16	0·17	0·17	0·17	0·18	0·18	0·18	0·18	0·18
1000	0·18	0·18	0·18	0·18	0·18	0·18	0·18	0·17	0·17	0·17

Platinum.

1	−0·02	−0·01	−0·01	−0·01	−0·01	0·00	0·00	0·00	0·00	0·00
10	+0·02	0·02	0·02	0·02	0·02	0·02	0·02	0·02	0·02	0·02
100	0·27	0·33	0·36	0·37	0·38	0·40	0·41	0·41	0·41	0·41
1000	0·46	0·46	0·46	0·46	0·45	0·45	0·45	0·45	0·45	0·45

Gold.

100	0·20*	0·21	0·22	0·23	0·24	0·25	0·26	0·28	0·30	0·31
1000	0·30	0·31	0·31	0·30	0·31	0·31	0·31	0·30	0·31	0·32

* Current of 500 milliamperes passed for 5 secs. to passivate the electrode.

Palladium.

100	0·01	0·02	0·02	0·02	0·02	0·02	0·02	0·02	0·02	0·02
1000	0·07	0·07	0·07	0·07	0·07	0·07	0·07	0·07	0·08	0·08

Remarks on Individual Electrodes.

Generally speaking, the purity of the electrodes is a matter of little importance, and although in this work electrodes having a high standard of purity were used, identical results were obtained in the few cases where parallel experiments were performed on less pure metals. The gas carbon electrodes were small rods obtained from Le Carbone Cie, and the graphite electrodes were manufactured by the Acheson Co. of Niagara Falls.

Little need be said about the attackable electrodes. Copper and mercury become coated with cuprous and mercurous chlorides respectively, and no metal can be detected in solution. Silver is coated with a thick deposit, white next the metal and purple on the surface. These phenomena appear to indicate a reducing action of the chlorine ions similar to that of hydrogen peroxide or permanganates. The purple colour of the silver chloride may be due to a colloidal solid solution of metallic silver comparable with Purple of Cassius.

Thallium.—The behaviour of this metal is peculiar and needs further study. Sometimes it behaves as a passive electrode and current passes freely, whilst at other times the same electrode under apparently similar conditions behaves as a valve electrode, but does not show the high back electromotive force typical of most valve electrodes.

Gold.—The back electromotive force was strongly negative and the metal dissolved freely without evolution of gas until the current density was raised to 200 milliamperes per sq. cm. When this point was reached, the back electromotive force rose more than 0·5 volt in three seconds, dissolution of the metal almost ceased, and chlorine was evolved freely. Under these conditions the gold was undoubtedly in the passive state. On reducing the current density, this condition persisted until the current was less than 10 milliamperes, when the active state returned suddenly.

Gas Carbon.—From a technical point of view, the carbon anodes, including graphite, are certainly the most important in connexion with chloride solutions, and from a theoretical point of view their behaviour is no less interesting.

With a fresh carbon rod, the overvoltage is at first negative owing to the free absorption of chlorine. Even when saturated, the overvoltage remains low (nearly zero) until a moderately high current density is applied, when it suddenly rises to more than 0·4 volt. After the electrode has been used for some time at high current densities, the overvoltage tends to rise to a still higher value, but these higher values are erratic and unstable. The surface is dis-

integrated and has every appearance of having been graphitised to a depth of nearly half a millimetre. Bubbles of gas emerge from the electrode long after the current has been stopped, showing the great pressures which must be produced within the substance. A process in general use in large scale work to minimise this disintegration consists in steeping the electrode in melted paraffin wax. Electrodes treated in this way were used in obtaining the results shown under the heading Carbon 2. It will be seen from the tables that the effects of waxing are to prevent absorption and to raise the overvoltage almost immediately to values of more than 0·4 volt even at low current densities. At very high current densities the overvoltage is lower than that of the unwaxed electrodes, and at the same time disintegration appears to be greater.

Acheson Graphite.—These electrodes also have been examined both in the unwaxed and the waxed condition. The absorption of chlorine is evidently very slight, but the overvoltage soon rises to a very persistent value of about 0·18 volt and only after long use at very high current densities is the steady value of 0·45 volt obtained with the unwaxed electrodes. On the other hand, the waxed electrodes only show the lower value at very low current densities, and a very rapid rise to a moderately constant value of more than 0·4 volt when the current density is raised. At high current densities a further rapid rise occurs to nearly 0·7 volt and this value is very constant and persistent although the surface is disintegrating. It is evident, therefore, that carbon shows four definite overvoltages —zero, 0·18, 0·45 and 0·70 volt—with rapid transitions from one to another.

Antimony, Tantalum, and Tungsten.—These metals show the phenomena of valve action. An insulating film rapidly forms on the surface, black in the case of antimony and bronze-coloured in the cases of tantalum and tungsten. At the same time the back electromotive force rises to a high value, 4 volts or more.

Chromium behaves in a peculiar manner. When no current is passed, its potential referred to a chlorine electrode is about −0·8 volt. When a small current is passed, this potential rises to −0·09 volt, but when the current is increased the potential falls regularly, as shown in the table. These potentials are remarkably constant and are more accurately reproducible than those of any other electrode used in these experiments. No gas is liberated, but chromic acid is formed. No chromium salt could be detected. It is doubtful whether this can be looked upon as a case of passivity or not. The rise of single potential seems to indicate passivity and the dissolution of the metal as chromic ion is prevented, but at the same time the formation of chromate ion is induced.

Rhodium.—According to Roscoe, of all the platinum metals, rhodium is the most easily attacked by chlorine. This statement certainly does not hold if anodic chlorine is used, for no evidence of any action could be detected, whereas palladium under certain circumstances dissolves freely. Its overvoltage is not very definite except at low current densities, when it is nearly zero, and at high current densities, when it approaches the value 0·3 volt. Between these limits, the values vary too much with current density for any trustworthy conclusions to be drawn.

Palladium like gold shows the typical behaviour of a passive metal. At low current densities the metal dissolves readily, giving a deep yellow solution. No gas is liberated and the single potential is about 0·5 volt below that of a chlorine electrode. When the current density is increased from 50 to 100 milliamperes per sq. cm., dissolution of the electrode suddenly stops, gas is liberated and the single potential rises by more than 0·5 volt. When the current density is reduced, the active state is restored with similar suddenness. In the passive condition, the overvoltage is always low and may be taken as approximately zero.

Iridium.—When first used, the overvoltage of an iridium electrode is low until a current of 50 milliamperes is passed. At this stage, a rapid rise occurs and at higher current densities the overvoltage may exceed 0·2 volt, but this high value is transient and a constant value of 0·18 volt is soon attained. After use, small patches of the electrode were found to be slightly "frosted," and microscopic examination showed that this frosted appearance was due to minute, crater-like formations similar to those of which photographs have been shown (T., 1914, **105**, 2427). A small quantity of gas issues from these patches after the current has been cut off.

Platinum.—This metal shows three clearly marked overvoltages—zero, 0·18 and 0·45 volt—the transition from one to another being remarkably rapid and definite. The very low and constant overvoltage at low current densities renders this metal very suitable to moderated electrolytic chlorinations. When the current density reaches 200 milliamperes per sq. cm. a sudden rise of overvoltage occurs from nearly zero to 0·45 volt, and this value persists up to 1000 milliamperes per sq. cm. If now the current density is doubled, the anode surface becomes broken (frosted) and the overvoltage diminishes to 0·18 volt. This value persists at high and at medium current densities, and the higher value can only be restored by removing the electrode, cleaning and repolishing. The dependence of high overvoltages on conditions which admit of very high internal gaseous pressures is thus well illustrated.

The absorption of chlorine under pressure is also well shown

by coating one side of the electrode with sealing wax about 1—2 mm. thick. When the current is passed, the electrode surface expands and exerts a considerable force on the backing of sealing wax, which is sometimes even broken by its tendency to curl with the convex metallic surface. When the current is interrupted, gas escapes from the electrode for several minutes and the metal slowly regains its initial shape.

It appears from these results that for moderate electrolytic chlorination, platinum electrodes, preferably platinised, with low current densities are suitable, whereas for very powerful chlorinations, waxed graphite electrodes are the only electrodes capable of giving the requisite, high overvoltages.

Discussion of Results.

The most striking feature of these results is their remarkable resemblance to those obtained for hydrogen overvoltages. The number of cases where the hydrogen and chlorine overvoltages are identical is far too great to be accidental, and the necessary conclusion from this is that the law previously suggested—elements in the same group of the periodic system show the same hydrogen overvoltages—must be extended to include chlorine overvoltages. In other words, hydrogen and chlorine overvoltages are the same functions of the valency of an electrode.

The following table of chlorine overvoltages may be compared with that of hydrogen overvoltages given in T., 1916, **109**, 1115 (metals which have the overvoltage of a group to which they do not properly belong are placed in brackets).

Group 0.—Typical overvoltage, 0·0 volt; (carbon), (rhodium), (iridium), (palladium), (platinum).

Group I.—Typical overvoltage, 0·35 volt; gold, (thallium).

Group II.—Typical overvoltage, 0·7 volt; (carbon).

Group IV.—Typical overvoltage, 0·45 volt; carbon, (platinum).

Group VI.—Typical overvoltage, 0·3 volt; (rhodium).

Group VIII.—Typical overvoltage, 0·18 volt; (carbon), iridium, platinum.

It is noteworthy that only waxed graphite is capable of showing the high overvoltage of a bivalent element, and that the higher values generally are more difficult to obtain than those in the case of hydrogen overvoltages. This is due partly to the great chemical activity of chlorine and partly to its greater solubility in the electrolyte as compared with hydrogen. Both factors tend

to prevent the development of the high pressures necessary for high overvoltages.

A further interesting point arises when chlorine and hydrogen overvoltages are compared with oxygen overvoltages. It was suggested, somewhat tentatively (T., 1916, **109**, 1117), that if the single potential of the hypothetical hydroxyl electrode is taken as standard in place of that of the oxygen electrode, anodic (hydroxyl) overvoltages show a marked resemblance to hydrogen overvoltages. The data available at the time were considered insufficient to justify a definite conclusion as to the identity of hydrogen and hydroxyl overvoltages, but in the light of the present work it appears evident that hydrogen, hydroxyl, and chlorine overvoltages are all identical and are completely determined by the valency of the electrode.

In this connexion the position of graphite in group VIII of the above table calls for comment. The overvoltage of 0·18 volt, which hitherto has only been observed in the case of elements of group VIII, is so definitely and persistently shown by graphite *that one is forced to the conclusion that graphite is behaving as* an octavalent element. The *atom* of graphite therefore must contain a double *nucleus with at least the outer* rings of valency electrons of two carbon atoms rotating about this double nucleus. This raises a tempting, if dangerous, field of speculation, and the following two examples may be given as illustrations of the many conclusions which could be drawn :—

1. The tendency to form long carbon chains in organic compounds may be due to this capacity of the carbon nuclei to coalesce.

2. The abnormal behaviour of the first member of a homologous series may be due to the presence of a true carbon atom, whilst the next member of the series would contain a double carbon or graphite atom. Thus methyl alcohol would still be $CH_3{\cdot}OH$, whilst ethyl alcohol might be written $(Gr)H_5{\cdot}OH$. The quantity of heat evolved when amorphous carbon changes to graphite indicates that the carbon atoms in graphite are more closely bound together than those in amorphous carbon, and the increase in density points to the same conclusion.

Summary and Conclusions.

The more important points so far established with relation to overvoltage may now be summarised.

1. Overvoltage is only produced when gases under high pressures are liberated at an electrode.

2. Overvoltage is the same whatever gas is liberated, whether carrying a positive or negative charge. Hence the increase of

potential produced by removing an electron from an ion already containing x positive charges is the same arithmetically as the decrease of potential produced by adding an electron to an ion already containing x negative charges.

3. The nature of the electrode surface, material of the electrode, nature and solubility of the gas liberated, current density, time, etc., are all factors in determining the gaseous pressures set up in the electrodes, and hence indirectly take part in the determination of the composition of the compounds responsible for overvoltage.

4. Overvoltage is independent of the particular element chosen as electrode, except in so far as it is indirectly affected by (3) above, but is dependent on the valency of that element.

It seems probable, therefore, that the overvoltage compounds carry an excess (or deficiency) of electrons and that the addition of each electron produces a definite increment in the single potential; this increment is dependent only on the number of loosely bound, valency electrons present in the atom of the electrode or ion of the overvoltage compound.

This leads naturally to the question of the normal single potentials of the elements and their relations to each other, and work is in progress along these lines, which, although not far advanced at present, has given good grounds for the statement of the following law:—

The single potentials of the elements are periodic functions of their atomic numbers.

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LXI.—*The Stability of Tautomeric Formaldehyde-phenylhydrazones.*

By NEVIL VINCENT SIDGWICK and ELINOR KATHARINE EWBANK.

BAMBERGER AND SCHMIDT (*Ber.*, 1901, **34**, 574, 2001) have shown that a series of substitution products of the phenylhydrazone of formaldehyde, of the type CHR:N·NHPh, occur in two modifications, which are certainly different in solution as well as in the solid state (see Sidgwick, T., 1915, **107**, 678), and are very probably *cis-* and *trans*-isomerides. They find that with such substances one form may be obtained by crystallisation from alcohol, and the

other from light petroleum. From this they infer that the stability of the form is determined by the solvent with which it is in contact. Dimroth (*Annalen*, 1910, **377**, 136) accepts this conclusion, and explains its apparent contradiction to the van't Hoff-Dimroth law (which makes the stability independent of the solvent) by assuming that the substances are polymerised in one solvent. It is easy to show that this explanation will not hold: if we take polymerisation into account, the van't Hoff-Dimroth equation assumes a somewhat different form, but still gives the stability as independent of the solvent. The only condition under which the solvent can determine the stability is when the heat of transformation is so small as to be comparable with that developed when the crystals are wetted with one or other solvent. Only one such case is known for certain, but this curiously is a substance of the same type as Bamberger and Schmidt's products, namely, the phenylhydrazone of acetaldehyde (Lockemann and Liesche, *Annalen*, 1905, **342**, 14; Laws and Sidgwick, T., 1911, **99**, 2085). It seemed therefore not impossible that the formaldehydephenylhydrazones offered another example of this peculiarity, and it was interesting to examine their behaviour from this point of view.

Two of these compounds were prepared and investigated, benzoylformaldehydephenylhydrazone (phenylglyoxalphenylhydrazone), $C_6H_5{\cdot}CO{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_5$, and nitroformaldehydephenylhydrazone, $NO_2{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_5$.

I. *Phenylglyoxalphenylhydrazone.*

This was prepared by Bamberger and Schmidt's method (*loc. cit.*). According to these authors, the α-form, obtained from benzene or light petroleum, melts at 114—117°, and the β-form, from alcohol, at about 138°.

The crude product from benzoylacetic ester and the diazonium salt (which is mainly the β-form) was boiled for several hours with light petroleum (b. p. 60—80°) until it was all dissolved. On cooling, short orange prisms of the α-form separated out, which melted at 111—112°.

Mere recrystallisation of this from alcohol was usually insufficient to cause any serious conversion into the β-form. A better method is to digest the crystals for several hours at 40—55°, or for a few days in the cold, with insufficient alcohol to dissolve them. The remaining crystals on drying were found to melt at 132—133°.

An attempt was made to distil the α-form under diminished pressure. At 23 mm. it came over with considerable decomposition at 215—230°, and condensed to an orange mass melting at 120°.

On distillation of the α-form with steam the compound came over slowly, separating from the distillate as a pale yellow, flocculent precipitate which melted at 134—135°, and appeared to be the pure or nearly pure β-form. But when this was digested with a little alcohol for several hours at 32°, its melting point rose to 145—146°. This seemed the most satisfactory method of obtaining the β-compound, and was that subsequently adopted. The exact melting point varied slightly with different preparations, but 145—146° was the highest observed, and is presumably the melting point of the pure β-modification.

In order to determine whether the stability of the forms is really dependent on the solvent, several samples of the α-form, melting at 111—112°, were left in contact with small quantities of light petroleum and alcohol respectively at the ordinary temperature, and from time to time portions of the solid were removed, dried, and their melting points measured. In all cases the melting point rose gradually, the final values reached, and the time required, being :—

In alcohol, 1 month	141°.
,, 1 month (another experiment) .	138°.
In light petroleum, 15 hours . . .	127°.
,, ,, 1 month . . .	133°.

It is therefore evident that the β-form is stable *in contact with either solvent. The peculiar behaviour of the substance must be due to the fact that the change of each modification into the other in solution is slow, and that the proportion of the* α-form *is much larger in non-associated solvents than in alcohol.* Hence when the β-form is boiled with light petroleum a solution is ultimately obtained which contains a large excess of the α-modification, and if this is rapidly cooled, the α-form crystallises out before it has time to change back into the β-form. But if sufficient time is given for the change, by leaving the crystals in contact with the solvent, the β-form is the ultimate product, whatever solvent is used. On distillation of the α-form with steam, the conversion into the β-form is nearly complete, so that the α-form must be almost absent from the vapour, or the conversion in water unusually rapid.

The exact melting point of any given sample varies with the rate of heating, and it is evident that the transformation is fairly rapid in the fused state. We were able to determine the natural freezing point by heating some of the substance in a test-tube containing a thermometer, in a bath of which the temperature was very slowly raised. Whether the α-form (m. p. 112°) or the β-form (m. p. 135°) was used, the last crystals were found to disappear at 128·5°.

The solubilities were measured by the synthetic method in alcohol, benzene, and *n*-heptane. In alcohol, the only form the solubility of which can be measured is the β, since the α is transformed into this before saturation is reached. But with benzene and heptane it is possible to measure the solubility of both forms in the same tube. If the tube is heated until all is dissolved, and then cooled rapidly, the orange crystals of the α-form separate, and the temperature can then be observed at which these are all dissolved; whilst if the tube is left for some time, a yellow powder of the β-form appears, and the solubility of this form can now be measured.

It is obvious that with a substance of this kind we might measure for each form two solubilities; (*A*) when the solution contains only that form, and (*B*) when it contains a mixture of the two in chemical (allelotropic) equilibrium. With these substances the isomeric change is too rapid at temperatures above the ordinary for it to be possible to measure (*A*), and it was only (*B*) that we could hope to determine.

The results are given in the following table, the first column indicating the number of grams of substance in 100 grams of solution. They cannot be made very accurate, because the chemical equilibrium is not completely established for a long time, but they give an approximation to the true values.

Solubility of Phenylglyoxalphenylhydrazone.

In Ethyl Alcohol.		In Benzene.			In Heptane.		
Per cent. (β-form)	Temp.	Per cent.	Temperature. α-form	β-form	Per cent.	Temperature. α-form	β-form.
(100·0	128·5°)	(100·0	—	128·5°)	(100·0	—	128·5°)
90·2	113·5	89·8	—	115·0	55·9	96·0°	113·0
74·9	103·4	70·8	75·3°	98·0	35·4	94·0	111·0
55·2	98·0	45·0	56·0	79·5	17·0	84·7	103·2
39·5	93·5	38·6	50·0	74·3	10·1	75·8	93·5
19·6	83·4	30·2	40·8	67·2	4·63	58·2	80—81
8·8	70·0	19·9	29·0	59·8	1·82	—	71—72
		10·4	8·0	44·2			
		4·8	—	26·0			

In benzene, the solubility of the α-form could not be determined at the highest temperatures, as it was converted into the β before saturation was reached; whilst at the lowest concentrations in heptane the exact temperatures were difficult to measure, owing to the small quantity of crystals which separated.

It can easily be shown that the ratio of the solubilities (if they are small) of the two forms of a substance in contact with the allelotropic solution must be the same at a given temperature in any solvent (for an example of this, see Chattaway and Lambert, T., 1915, **107**, 1781). To test this point, the solubilities were measured

in a thermostat at 32°, the hydrazone (either form) being stirred with the solvent until equilibrium appeared to be reached. The solutions were analysed by evaporating off the solvent at 100°. It was found that the time required for the β-form to reach equilibrium was usually one hundred to one hundred and fifty hours, whilst the α-form could not be left more than eight or nine hours in the other solvents, and not more than two hours in *cyclo*hexane, before the solid began to change into the β-form. Hence the values for the α-form are all somewhat low, and that for *cyclo*hexane is no doubt much too low.

Solubilities at 32°.

Solvent.	Per cent. α-form	Per cent. β-form	Ratio.
Benzene	25·1	8·0	3·1
Heptane	1·7	0·55	3·1
Carbon tetrachloride	8·8	2·27	3·9
*cyclo*Hexane	(2·56)	1·56	(1·7)

It will be seen that there is fair agreement, except in the last solvent, where the α-value is certainly too low, and hence the ratio likewise.

If the benzene values are plotted on the same diagram as the solubility determinations in this solvent given in the first table, they will be seen to be several units per cent. higher. There is no doubt that the determinations in the thermostat are more trustworthy, because a longer time was given for the attainment of equilibrium. By interpolation from the solubility curves we can get values of the ratio at every 10°. These, although only approximate, for the reasons given, are worth recording.

	Solubility in Benzene.			Solubility in Heptane.		
Temp.	α-form	β-form	Ratio.	α-form	β-form	Ratio.
90°	—	—	—	24·5	8·1	3·0
80	77·2	45·7	1·7	12·6	4·2	3·0
70	63·0	33·2	1·9	8·20	1·80	4·6
60	49·8	23·0	2·2			
50	37·5	15·0	2·5			
40	28·4	9·3	3·1			
30	20·7	5·5	3·8			
20	15·0	4·0	3·8			

The values of the ratio are much higher in heptane, probably owing to the difficulty of allowing enough time for saturation.

In benzene a fairly regular curve for the ratio is obtained, which extrapolates to a value between 4 and 5 at 0°. It is to be remembered that the generalisation is only strictly true in dilute solution, which may explain the fall in the ratio as the solution becomes

more concentrated; though it is also possible that the substance is approaching its transition point as the temperature rises.

The solubilities of the two forms in benzene at about + 3° have been measured by the freezing-point method (Sidgwick, T., 1915, **107**, 678), and were found to be : α, 5·84, β, 0·322 per cent. (assuming that they are not polymerised in solution). Under these conditions isomeric change is practically excluded, and these may be taken *to be solubilities in sense (A), with only one form in solution.* This enables us to arrive at an approximate value of the proportions of the two forms at allelotropic equilibrium in benzene.

As we have seen, the ratio of the solubilities of the two forms at allelotropic equilibrium (sense B) at + 3° is between 4 and 5. Let us assume it to be 4; and let the ratio of the concentrations $\alpha : \beta$ in benzene solution at + 3° be k. Then as we know that the percentage of α-form in solution in equilibrium with the solid α-form is 5·84, it follows that at allelotropic equilibrium there is also present in solution $5{\cdot}84/k$ per cent. of the β-form. In the same way in a *solution saturated with the solid β-form* we have 0·322 per cent. of the β-, and $0{\cdot}322 \times k$ per cent. of the α-form. Thus the total concentrations at equilibrium (sense B) are :—

Solution saturated with α- : $5{\cdot}84 + 5{\cdot}84/k = x$
" " " β- : $0{\cdot}322 + 0{\cdot}322 \times k = y$

The ratio $x/y = 4$, so that we have a quadratic for k, the value of which is found to be 4·5. If we assume the ratio to be 5 instead of 4, k will be 3·6. Taking the mean value $k = 4$, it follows that in benzene solution at + 3° there is at equilibrium approximately 4 times as much α- as β-form.

This also enables us to calculate the value of the van't Hoff-Dimroth constant G for this substance at + 3° :—

$$G = \frac{\text{Concentration of the } \beta\text{-form at equilibrium}}{\text{Concentration of the } \alpha\text{-form at equilibrium}} \times \frac{\text{Solubility of the } \alpha\text{-form}}{\text{Solubility of the } \beta\text{-form}}$$

$$= \frac{1}{4} \times \frac{5{\cdot}84}{0{\cdot}322} = 4{\cdot}5.$$

II. *Nitroformaldehydephenylhydrazone.*

The crude product obtained by Bamberger's method from nitromethane was freed from the nitroformazyl mixed with it by dissolving it in the cold in sodium hydroxide solution, and adding concentrated hydrochloric acid until a definite red precipitate was formed. This was filtered off, and excess of hydrochloric acid added to the filtrate. Five grams of crude product gave 3·6 grams of the β-hydrazone melting at 83·5° (Bamberger and

Schmidt, 84·5—85·5°). 2·8 Grams of this were warmed with 5 c.c. of benzene for half an hour, by which time solution was complete, and on cooling 2 grams of the α-form, m. p. 74° (Bamberger and Schmidt, 74·5—75·5°) were obtained.

Samples of the α-form were put in test-tubes with small quantities of alcohol, benzene, and carbon tetrachloride respectively. After three days at 32°, they all showed signs of considerable decomposition, except the sample in contact with alcohol, which had been seeded with a trace of the β-form. In this the liquid had solidified to a mass of the β-form, m. p. 82—84°. The same results occurred in another set, after a week at the ordinary temperature. In carbon tetrachloride, after two months at the ordinary temperature, a distinct yellow coating of the β-form was visible on the sides of the tube, although it could not be separated from the partly decomposed mass well enough for its melting point to be determined.

The instability of the compound made further investigation impossible; but these results are enough to show that with this hydrazone, as with the preceding one, the β-form is stable in contact with non-associated as well as with associated solvents. We may fairly assume that the same is the case with the other hydrazones examined by Bamberger and Schmidt.

One of us (E. K. E.) has received a grant from the Department of Scientific and Industrial Research, for which she wishes to express her thanks.

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OXFORD. [*Received, February 23rd*, 1921.]

LXII.—*The Chemistry of the Glutaconic Acids. Part XII. The Simultaneous Occurrence of* 1 : 2- *and of* 1 : 3-*Addition to "Nascent" Glutaconic Ester.*

By CHRISTOPHER KELK INGOLD and JOCELYN FIELD THORPE.

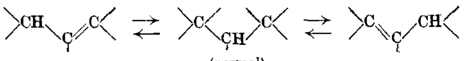
IN the previous parts of this series it has been shown that the glutaconic acids afford examples of a kind of tautomerism which, although of a fundamental nature, has hitherto passed unrecognised. This tautomerism is of the type associated with the "three-carbon system," and may be compared with keto-enolic and ketimino-enamic tautomerism in the following way :

$$\text{keto-enolic} \quad >\text{CH}\cdot\overset{|}{\text{C}}\text{:O} \rightleftarrows >\text{C:}\overset{|}{\text{C}}\cdot\text{OH}$$

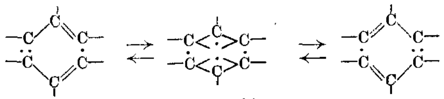
$$\text{ketimino-enamic} \quad >\text{CH}\cdot\overset{|}{\text{C}}\text{:N}- \rightleftarrows >\text{C:}\overset{|}{\text{C}}\cdot\text{NH}-$$

$$\text{three-carbon} \quad >\text{CH}\cdot\overset{|}{\text{C}}\text{:C}< \rightleftarrows >\text{C:}\overset{|}{\text{C}}\cdot\text{CH}<$$

The great difference between three-carbon tautomerism and the other varieties is clearly one of symmetry. Thus, when the mobile hydrogen atom in a keto-enolic system passes from carbon to oxygen, it must at some moment during the transit become attached to the central atom of the tautomeric grouping; but, owing to the unsymmetrical character of the grouping, this attachment can never constitute more than a very fleeting phase of the tautomeric interchange: the forces called into play will quickly draw the mobile atom either to the one side or to the other. In the case of the three-carbon system, on the other hand, the state in which the mobile hydrogen atom has become attached to the central carbon atom is the symmetrical one; the forces acting on the mobile atom will therefore be symmetrically arranged and will tend to create a condition of equilibrium. This symmetrical or "normal" state is in very many respects similar to the centric phase of the tautomerism of aromatic compounds. Both phases are in equilibrium with unsaturated phases, which, to judge by the properties of the substances, are in both cases relatively transient:



(normal)



(centric)

In glutaconic acid itself the normal state is so much more stable than the unsaturated state that it may be regarded for most purposes as the permanent condition of the substance. The effect of substitution by alkyl groups is two-fold. In the first place, substitution in the α-position disturbs the symmetry of the molecule, and therefore tends to reduce the permanence of the normal form which depends for its stability on an equilibrium of forces. Secondly, substitution in any position, but particularly at the central carbon atom of the system, reduces the velocity of tautomeric interchange,

in many cases to such a degree that the establishment of false or apparent equilibria becomes possible.

Thus, in the case of glutaconic acid itself, tautomeric interchange is rapid, and the substance can be isolated in one modification only, namely, the normal one. In the dissolved state, and in the form of its esters, it still appears to consist almost entirely of this modification, although, doubtless, there is always present the trace of the unsaturated isomeride necessary for the establishment of equilibrium.

In the case of β-methylglutaconic acid, on the other hand, both the *normal* and the *unsaturated* acids can be isolated in the pure condition, and, so far as is known, can be kept indefinitely. Even the liquid esters can be kept in the dark for years without any perceptible isomeric change, although in daylight the unsaturated ester undergoes conversion into the normal ester at quite an appreciable rate. (Part XI, T., 1919, **115**, 679.) Consequently, the esters of normal and of unsaturated β-methylglutaconic acid behave in ordinary laboratory experiments as stable isomerides rather than as tautomeric substances.

By studying these apparently stable isomerides it has been shown in previous parts of this series (Part IX, T., 1913, **103**, 1579; Part XI, *loc. cit.*) that the normal and the unsaturated esters differ sharply with regard to their capacity to form additive products with ethyl sodiocyanoacetate. Whilst the unsaturated ester, in common with almost all other αβ-unsaturated esters, readily forms a 1 : 2-additive product at the double bond, the normal isomeride reacts only very slowly, and forms a 1 : 3-additive product, as the semi-aromatic formula, which has been adopted as the best mode of representation for these compounds, requires :

$CH_2 \cdot CO_2Et$		$CH_2 \cdot CO_2Et$
CMe	$\xrightarrow{CHNa(CN) \cdot CO_2Et}$	$CMe \cdot CNa(CN) \cdot CO_2Et$
$CH \cdot CO_2Et$		$CH_2 \cdot CO_2Et$ (quickly formed)
$\cdot CH \cdot CO_2Et$		$CH_2 \cdot CO_2Et$
CHMe	" →	CHMe
$\cdot CH \cdot CO_2Et$		$CH(CO_2Et) \cdot CNa(CN) \cdot CO_2Et$ (slowly formed).

It is not possible to repeat these experiments and obtain parallel results with glutaconic ester itself owing to the great tautomeric mobility of this ester already referred to, and to the fact that only a trace of the unsaturated form is present in the equilibrium mixture. Nevertheless, the very high velocity of tautomeric interchange has made it possible to obtain an indication of the presence of the

unsaturated form. For, when glutaconic ester was heated with an alcoholic solution of ethyl sodiocyanoacetate (Part IX, *loc. cit.*), a condensation product was obtained in small yield, of which the main constituent was shown to consist of the 1 : 2-additive product derived from the unsaturated modification of the ester. The fact that this additive product was actually formed in recognisable amount, although small, was ascribed to the extremely mobile character of the tautomeric system. The tendency to the restoration of equilibrium, as it became disturbed by the removal of the reactive constituent, must have maintained the concentration of the latter at a nearly constant (although extremely low) value throughout the period of interaction.

Such evidence of the existence of the unobtainable, unsaturated form of glutaconic ester, and of the mobile equilibrium subsisting between it and the normal modification, appears rather incomplete, and needs to be substantiated. Now, although the unsaturated ester cannot be isolated, there is no obvious reason why its characteristics should not be studied by making use of the nascent condition of the substance.

The term "nascent" is here used in view of a very obvious analogy in inorganic chemistry. Gaseous hydrogen, as such, is a very feeble reducing agent. Its generation, however, takes place, when a metal dissolves in water, in two stages, and there is formed intermediately atomic hydrogen, which is a powerful reducing agent:

$$\mathrm{Na} + \mathrm{H_2O} \longrightarrow \mathrm{NaOH} + \mathrm{H}.$$

$$2\mathrm{H} \underset{\longleftarrow}{\longrightarrow} \mathrm{H_2}.$$

Atomic hydrogen, as such, cannot be isolated, and therefore, in order to be used for reduction, must be employed in the nascent state, that is to say, must be generated in the presence of the substance to be reduced. Direct competition then takes place between the reducing reaction and the conversiou of atomic hydrogen into the stable, molecular form. If one regards the latter reaction as having a minute degree of reversibility, indicated by the symbol in the second equation (above), the analogy with glutaconic ester becomes complete.

In order, therefore, to make use of the unsaturated modification of *glutaconic ester in the nascent state, it is necessary to generate* this substance in the presence of a reagent with which it can combine. A method of accomplishing this has been indicated by one of us in a recent paper. It was there shown (this vol., p. 329) that the esters of β-hydroxy-acids readily eliminate water and pass into unsaturated substances under the action of a hot, alcoholic

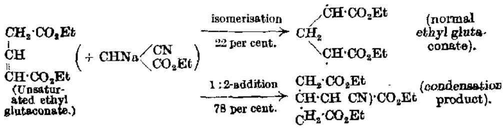
solution of ethyl sodiocyanoacetate. Therefore β-hydroxyglutaric ester, when treated in this way, should yield glutaconic ester *in its unsaturated form.* Under more usual conditions of formation this substance would quickly change into the normal modification :

$$CO_2Et{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2Et \longrightarrow \begin{array}{c} CO_2Et{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2Et \\ \downarrow\uparrow \\ CO_2Et{\cdot}\dot{C}H{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CO_2Et \end{array}$$

Here, however, the unsaturated ester would be produced in the presence of a reagent for unsaturated compounds, and combination with the reagent should ensue to an extent determined by the *velocity of this reaction in relation to that of the tautomeric change.*

Actually the velocity of the condensation reaction compares very favourably with that of the tautomeric interchange. A preliminary indication has been given elsewhere (this vol., p. 346) that, under the experimental conditions employed, the yield of the condensation product derived from the nascent unsaturated ester amounts to 65 per cent. of that theoretically possible. Calculated on the quantity of the nascent ester which can be shown (p. 498) to have been formed (this quantity is actually rather less than the theoretical amount) the proportion found as the condensation product derived from this substance amounts to as much as 78 per cent. of the total. The quantity simultaneously converted into the normal isomeride is consequently only 22 per cent.

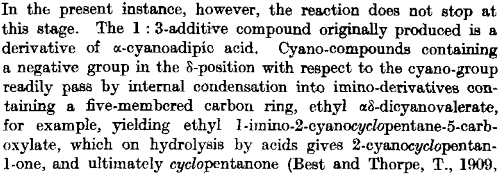
As it is not possible (Part XI, *loc. cit.*) to obtain from the normal, or, *to speak more accurately*, the *equilibrium*, ester a yield of condensation product amounting to more than a few units per cent. of the theoretical, even by using a large excess of the reagent, the production of 78 per cent. by the method just described undoubtedly constitutes one of the best examples yet recorded of the phenomenon of the nascent state amongst organic compounds. The competing reactions may be represented thus :



This condensation product is not the only one obtained. Th normal ethyl glutaconate formed enters partly into condensatio with ethyl sodiocyanoacetate to form a 1 : 3-additive product i accordance with the properties of normal esters as revealed b the study of normal β-methylglutaconic ester (Part XI, *loc. cit.*

In the present instance, however, the reaction does not stop at this stage. The 1 : 3-additive compound originally produced is a derivative of α-cyanoadipic acid. Cyano-compounds containing a negative group in the δ-position with respect to the cyano-group readily pass by internal condensation into imino-derivatives containing a five-membered carbon ring, ethyl αδ-dicyanovalerate, for example, yielding ethyl 1-imino-2-cyano*cyclo*pentane-5-carboxylate, which on hydrolysis by acids gives 2-cyano*cyclo*pentan-1-one, and ultimately *cyclo*pentanone (Best and Thorpe, T., 1909, **95**, 685).

The 1 : 3-additive product undergoes a similar internal condensation except that in this case a carbethoxyl group is eliminated (compare the formation of α-hydrindone derivatives by the imino-condensation; Mitchell and Thorpe, T., 1910, **97**, 2261). The imino-compound, ethyl 4-imino*cyclo*pentane-1 : 3-dicarboxylate, is not obtained as such owing to the use of mineral acid during the separation. This hydrolyses the imino-group, and ethyl *cyclo*pentan-1-one-2 : 4-dicarboxylate is the substance actually isolated :



The constitution of ethyl *cyclo*pentanone-2 : 4-dicarboxylate, except for an ambiguity * of minor importance, is proved by the fact that on hydrolysis it eliminates one carboxyl group and passes into *cyclo*pentanone-3-carboxylic acid, which has been prepared and characterised by Kay and Perkin (T., 1906, **89**, 1646).

As is almost invariably the case with reactions involving ethyl cyanoacetate, the quantitative separation of the products is complicated by the formation of a considerable proportion of acid-esters. The method of separation employed in the present instance is described in the experimental portion of this paper, and the results of a typical experiment are quoted in the table given below. In

* This arises from the fact that either of the two carbethoxyl groups could have been eliminated during the internal condensation. In each case, stereoisomeric products are possible. Any of these would respond to the ferric chloride test, and give *cyclo*pentanone-3-carboxylic acid on hydrolysis. However, the uncertainty as to the exact constitution and configuration of the substance isolated does not affect the main points dealt with in this paper.

this table the quantities of the various products are calculated as their equivalent weights (per cent.) of glutaconic ester.

An inspection of the table will show the experimental basis for the statement made on p. 496 that the nascent unsaturated ester is isomerised into the normal modification to the extent of 22 per cent, whilst condensation with the additive reagent occurs to the extent of 78 per cent. These figures are probably subject to slight corrections, as about one-half of the unidentified material was actually recovered, and was found to consist for the most part of substances which decomposed on distillation.

Another interesting ratio is that expressing the relative quantities of the products of 1 : 2- and 1 : 3-addition. These occur in the proportion of 78 to 9, or, approximately, 9 to 1. The simultaneous formation of such substances by the methods described in this paper appears to us a most convincing confirmation of the essentially tautomeric relationship subsisting between the normal and the unsaturated or labile modifications of the glutaconic acids, and of the semi-aromatic structures of the normal isomerides.

TABLE.

(*A*) *Total Material.*	Per cent. (of total material)
Not recovered / Recovered but not identified	9
Recovered, separated, and identified as pure products	91
Total......	100

(*B*) *Identified Material.*	Per cent. (of identified material)	
Unchanged ethyl β-hydroxyglutarate	9	8
Products from nascent ethyl glutaconate	91	83
Totals......	100	91

(*C*) *Products from Nascent Glutaconic Ester.*		Per cent (of products from glutaconic ester)			
(*a*) Normal ethyl glutaconate		13			
(*b*) Products of 1 : 3-*addition* :					
(i) Neutral ketonic ester	7				
(ii) Acid ketonic ester ...	2				
Total......		9			
Total......			22	20	18
(*c*) Products of 1 : 2-addition :					
(i) Neutral cyano-ester	48				
(ii) Acid cyano-ester ...	30				
Total......		78	78	71	65
Totals......			100	91	83

Experimental.

The condensation of ethyl β-hydroxyglutarate with ethyl sodiocyanoacetate was effected by the general method given previously (Ingold, this vol., p. 336).

The alcoholic suspension of sodium compounds, which had remained practically colourless throughout the course of the condensation, was mixed with water, and the esters were extracted with ether.

Ethyl Glutaconate.

The residue from the ether was distilled under reduced pressure, and the fraction containing the dicarboxylic esters refractionated several times. In this way, ethyl glutaconate, b. p. 118—125°/13 mm., was obtained in considerable quantity (Found: C = 57·65; H = 7·5. Calc., C = 58·1; H = 7·5 per cent.); on hydrolysis, it gave glutaconic acid, which was identified with a known specimen (Found: C = 46·0; H = 4·6. Calc., C = 46·1; H = 4·6 per cent.).

Ethyl β-Hydroxyglutarate.

The bulk of the remainder of the dicarboxylic ester fraction, b. p. 145—150°/13 mm., evidently consisted of unchanged ethyl β-hydroxyglutarate. It was identified by analysis (Found: C = 53·4; H = 7·8; Calc., C = 53·0; H = 7·9 per cent.) and by its behaviour with phosphorus pentachloride.

Ethyl ω-Cyanomethanetriacetate.

The less volatile fraction of the esters distilled almost entirely at 203—204°/13 mm., although a small amount suffered decomposition during the distillation. This fraction contained nitrogen, and obviously consisted of the above cyano-ester (Found: C = 56·2; H = 7·0. Calc., C = 56·2; H = 7·0 per cent.), since it gave methanetriacetic acid (m. p. 115°; Found: C = 44·1; H = 5·4. Calc., C = 44·2; H = 5·3 per cent.) on hydrolysis. (Ingold., *loc. cit.*, and this vol., p. 352).

Ethyl cyclo*Pentanone-2 : 4-dicarboxylate.*

The alkaline liquid containing the remaining condensation products was acidified, extracted with ether, and the extract washed with a solution of sodium carbonate. The residue obtained on evaporating the ether was dissolved in a solution of sodium hydroxide, treated with carbon dioxide, and the precipitated ester solidified by shaking, collected, and crystallised from ethyl alcohol. It separated in long needles melting at 78—79° (Found: C = 58·3; H = 6·9. $C_{11}H_{16}O_5$ requires C = 57·9; H = 7·0 per cent.).

The ester is extremely soluble in most organic solvents, but is only moderately soluble in methyl and ethyl alcohols at 0°. In aqueous alcohol it develops an intense blue colour when treated with ferric chloride. Its behaviour on hydrolysis is described on p. 501.

The *semicarbazone* slowly separated when an alcoholic solution of the ketonic ester was allowed to react with an aqueous solution of semicarbazide acetate. It crystallised from ethyl alcohol in long needles which melted at 160° (Found: C = 51·0; H = 6·5. $C_{12}H_{19}O_5N_3$ requires C = 50·5; H = 6·7 per cent.).

Ethyl β-Cyanomethylglutarate, $CN\cdot CH_2\cdot CH(CH_2\cdot CO_2Et)_2$.

The sodium carbonate washings obtained in the preparation of the ketonic ester were acidified with hydrochloric acid and shaken with ether. The extracted material was distilled under reduced pressure, and the distillate, after having been washed with a solution of sodium carbonate, purified by redistillation. The cyano-ester so prepared boiled at 158—160°/15 mm. (Found: C = 58·4; H = 7·3. $C_{11}H_{17}O_4N$ requires C = 58·1; H = 7·5 per cent.) and on hydrolysis yielded methanetriacetic acid.

Ethyl cyclo*Pentanone-3-carboxylate.*

A portion of that material which on distillation yielded cyanomethylglutaric ester was dissolved in an equal volume of cold, concentrated sulphuric acid; the mixture was poured after a few hours into ten volumes of water and boiled for seven hours. The acids were then extracted with ether, and re-esterified by treating at 100° for half an hour with ethyl alcohol (2 parts by weight) and concentrated sulphuric acid (1 part). The esterification was only partial, and the greater part of the material was recovered as acid esters. However, the neutral esters were isolated separately, and distilled under reduced pressure, when a small fraction was obtained, b. p. about 120°/14 mm., which apparently consisted of the ethyl ester of *cyclo*pentanonecarboxylic acid (Found: C = 61·9; H = 7·9. $C_8H_{12}O_3$ requires C = 61·6; H = 7·7 per cent.), as it gave this acid on hydrolysis.

Ethyl Methanetriacetate.

By far the largest quantity of the distillate had boiled at 160—175°/14 mm.

Further, the acid products of the esterification, when re-esterified by the ethyl alcohol-zinc chloride-benzene process, yielded a neutral ester having the same boiling point. A preliminary examination having indicated that the two esters were identical, they

were combined and twice redistilled. The pure ethyl methanetriacetate, thus obtained, boiled at 172—173°/14 mm. (Found: C = 56·8; H = 8·0. $C_{13}H_{22}O_6$ requires C = 56·9; H = 8·0 per cent.), and, on hydrolysis with hydrochloric acid, produced the corresponding acid.

Methanetriacetic Acid.

A mixture of the ester (1 vol.) and concentrated hydrochloric acid (10 vols.) was heated for seven hours to expel ethyl alcohol, the product was concentrated on the steam-bath, and the residual syrupy acid dissolved in ether. The material obtained from the ethereal solution melted at 113·5—114·5° and consisted of methanetriacetic acid in an almost pure condition (Found: C = 44·3; H = 5·3. Calc., C = 44·2; H = 5·3 per cent.). It was identified by direct comparison, and by means of its dianilic acid, m. p. 192° (Ingold, *loc. cit.*).

The same acid was obtained when ethyl β-cyanomethylglutarate mixed with cold, concentrated sulphuric acid (1 vol.) was poured, after keeping for twelve hours, into water (4 vols.), the liquid boiled for four hours under a short condenser, and the acid product extracted with ether. It was crystallised from dry ether, and identified by the method of mixed melting point, and by conversion into its dianilic acid (*loc. cit.*).

cyclo*Pentanone-3-carboxylic Acid.*

This acid was obtained when either its own ester or that of *cyclo*pentanone-2 : 4-dicarboxylic acid was boiled with sulphuric acid (8 per cent.; 10 parts by weight) for three hours, and the organic acid extracted with ether. Owing to the small amount of material at our disposal we were unable to purify the acid by Kay and Perkin's method (*loc. cit.*). The composition of the acid was therefore controlled by an analysis of the silver salt (Found: C = 30·9; H = 3·0; Ag = 46·3. $C_6H_7O_3Ag$ requires C = 30·6; H = 3·0; Ag = 46·0 per cent.), and its identity determined by means of its oxime, m. p. 140—141° (Found: C = 50·7; H = 6·6. Calc., C = 50·4; H = 6·3 per cent.), and semicarbazone, m. p. 190° (Found: C = 45·6; H = 5·9. Calc., C = 45·4; H = 5·9 per cent.), these being the temperatures recorded by Kay and Perkin.

Our thanks are due to Mr. L. Nickolls, who very kindly prepared the ethyl β-hydroxyglutarate used in this research.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, February 17th, 1921.*]

THE Council has ordered the following report and list of Physico-chemical Symbols to be printed in the Journal.

International Physico-chemical Symbols.

(AUTHORISED FOR PUBLICATION BY THE COUNCIL OF THE CHEMICAL SOCIETY.)

AT the meeting of the Council of the International Association of Chemical Societies, held in Brussels in September, 1913, it was decided that the International Commission for the Unification of Physico-Chemical Symbols "shall appoint a small 'Working Committee' of five members, not necessarily members of the Council, to receive and consider the reports of the National Committees, and further to suggest methods for the organisation and carrying out of future work." In accordance with this decision, the President of the International Commission (the late Sir William Ramsay) nominated the following gentlemen to serve on the Working Committee, namely, Sir William Ramsay (Chairman), Dr. Friedrich Auerbach, Professor P. A. Guye, Professor P. J. Walden, and Professor Alex. Findlay (Secretary), and these nominations were approved by the Commission.

In accordance with the decision of the International Commission, approved by the Council (Report, 1913, p. 27), the list of symbols recommended by the Commission was sent to the different societies affiliated with the International Association of Chemical Societies, as well as to the Ausschuss für Einheiten und Formelgrössen and the International Electrotechnical Commission, and the request was made that these societies or bodies should intimate to the Secretary any criticisms or suggestions which they might have to make regarding the symbols recommended.

The criticisms and suggestions received were considered at a meeting of the Working Committee held in Paris on May 29th and 30th, 1914. At this meeting, Dr. Charles Marie was also present by invitation of the Chairman.

At the outset, the following general principles were adopted:

1. The decisions of the Committee shall be restricted to symbols for quantities of chemical or physico-chemical importance.

2. In respect of symbols for quantities used, more especially in mathematics, physics, and the various branches of applied mathematics and physics, the Committee shall restrict itself to *noting* the symbols which have been recommended or adopted by the

scientific bodies specially interested in these quantities. With regard to the latter, it was resolved to include in the list of symbols only those about which there is general agreement among the *specially competent bodies*.

3. The decisions of the Committee shall be restricted to symbols for quantities, and shall not extend to signs for the names of units.

4. The Committee considers it to be inadvisable that any attempt should be made to *compel* authors to use the symbols which the Committee recommends. Every means, however, should be taken to *encourage* the use of these symbols, which would be revised at such times and in such ways as might appear to the Commission to be advisable.

5. With regard to the symbols for quantities which are employed in different branches of pure or applied science, the Committee considers that it is not possible in every case to obtain agreement between the different sciences. It is of opinion, therefore, that the symbols suggested should be such as might find general acceptance by chemists and physico-chemists.

6. The Committee recommends that in every case authors should express their results in C.G.S. units.

On the basis of these general principles, the Committee drew up, *for the approval of the International Commission, the list of* symbols given below. This list of symbols was circulated among the members of the Working Committee, and was returned to me approved and initialled by Sir William Ramsay, Dr. Auerbach, Professors Guye and Walden, and Dr. Marie. It was the intention, after taking account of any remarks made by the members of the Committee, to circulate the final list for signature by the members of the Committee, but the outbreak of war prevented *this from being done*. These remarks have, however, been taken account of in the list given below, which may be taken as being practically identical with that initialled by the individual members of the Committee.

In accordance with a recommendation of the Working Committee, it has been thought well to append to the list of symbols the reasons for the choice of symbol made by the Committee in certain debated cases.

ALEX. FINDLAY,
Secretary to the Working Committee.

List of Symbols Recommended by the Working Committee of the International Commission for the Unification of Physico-chemical Symbols (1914).

1. *Mathematical Symbols.*

	Usual symbol.	Alternative symbol.
Base of natural (Napierian) logarithms ...	e	
Diameter	d	
Radius	r	
Ratio of circumference to diameter	π	
Summation	Σ	
Variation	δ	
Total differential	d	
Partial differential	∂	

2. *Universal Constants.*

Acceleration due to gravity	g	
Mechanical equivalent of heat	J	
Avogadro's constant [number of molecules in 1 gram-molecule (mole)]	N	
Gas constant per mole	R	
Faraday's constant (number of coulombs per gram-equivalent of an ion)	F	
Charge on an electron	e	

3. *General Physics and Chemistry.*

Length	l	
Height	h	
Mass	m	
Time	t	
Volume	v, V	
Density (mass per unit volume)	d	D
Pressure	p, P	
Concentration	c, C	
Mole fraction	x	
Critical constants: pressure, volume, temperature (centigrade), temperature (absolute), density	p_c, v_c t_c, T_c d_c	
Reduced quantities: pressure, volume, temperature, density	p_r, v_r t_r, T_r, d_r	
van der Waals's constants	a, b	
Fluidity	ϕ	
Viscosity	η	
Surface tension	γ	σ
Diffusion coefficient	Δ	
Atomic weight	A	
Molecular weight	M	
Velocity coefficient of reaction	k	
Equilibrium constant	K, (K_c, K_p)	
van't Hoff coefficient	i	
Degree of dissociation (electrolytic, thermal, etc.)	α	

4. *Heat and Thermodynamics.*

	Usual symbol.	Alternative symbol.
Temperature (centigrade)	t	θ
Temperature (absolute)	T	
Critical temperature	t_c, T_c	
Reduced temperature	t_r, T_r	
Critical solution temperature	t_{cs}, T_{cs}	
Quantity of heat	Q	
Entropy	S	
Specific heat	c	
Specific heat at constant pressure	c_p	
Specific heat at constant volume	c_v	
Ratio of specific heats, $c_p : c_v$	γ	
Molecular heat	C	
Molecular heat at constant pressure	C_p	
Molecular heat at constant volume	C_v	
Latent heat per gram	l	
Latent heat per mole	L	
Maximum work (diminution of free energy)	A	

5. *Optics.*

	Usual symbol.	Alternative symbol.
Wave-length of light	λ	
Refractive index	n	n_r
Specific refractive power (Gladstone and Dale)	r_G, $[r_G]^{t°}_{\lambda}$	
Specific refractive power (Lorentz and Lorenz)	r_L, $[r_L]^{t°}_{\lambda}$	
Molecular refractive power	R_G, R_L; $[R_G]^{t°}_{\lambda}$, $[R_L]^{t}_{\lambda}$	
Angle of optical rotation	α	
Specific rotatory power	$[\alpha]$	
Molecular rotatory power	$M[\alpha]$	
Specific magnetic rotation	$[\omega]$	
Molecular magnetic rotation	$M[\omega]$	

6. *Electricity and Magnetism.*

	Usual symbol.	Alternative symbol.
Quantity of electricity	Q	
Current intensity	I	
Resistance	R	W
Electromotive force	E	
Electrode potential, or discharge potential of an ion	E	ϵ
Electrode potential referred to the normal hydrogen or normal calomel electrode respectively, the potential of which is taken as zero	E_h, E_c	ϵ_h, ϵ_c
Normal potential, *i.e.*, the electrode potential referred to the normal hydrogen or normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration	${}_0E_h$, ${}_0E_c$	${}_0\epsilon_h$, ${}_0\epsilon$
Dielectric constant	ϵ	
Conductivity (specific conductance)	κ	
Equivalent conductivity	Λ	
Equivalent conductivity at different dilutions—volumes in litres containing 1 gram-equivalent	Λ_{10}, Λ_v, Λ_∞	

6. *Electricity and Magnetism*—(continued).

	Usual symbol.	Alternative symbol.
Equivalent conductivity of kation and of anion	Λ_k, Λ_a	
Equivalent conductivity of specified ions...	$\Lambda_{K'} \Lambda_{Cl'}$	
Molecular conduotivity	μ	
Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm.	U_k, U_a	
Transport number of kation and of anion ...	n_k, n_a	
Magnetic permeability	μ	
Magnetic susceptibility	κ	

List of Symbols, Arranged Alphabetically.

Symbol.	Name of quantity.
A	Atomic weight; maximum work.
a	Van der Waals's constant.
b	Van der Waals's constant.
C	Concentration; molecular heat.
c	Concentration; specific heat.
C_p, C_v	Molecular heat at constant pressure, and at constant volume.
c_p, c_v	*Specific heat at constant pressure, and at constant volume.*
D	Alternative symbol for density.
d	Diameter; total differential; density.
d_c	Critical density.
d_r	Reduced density.
E	Electromotive force; electrode potential.
e	Base of Napierian logarithms; charge on an electron.
E_h, E_c	Electrode potential referred to the normal hydrogen or the normal calomel electrode, respectively, the potential *of which is taken as zero.*
${}_0E_h, {}_0E_c$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration.
F	Faraday's constant (number of coulombs per gram-equivalent of an ion).
g	Acceleration due to gravity.
h	*Height.*
I	Current.
i	Van't Hoff's coefficient.
J	Mechanical equivalent of heat.
K	Equilibrium constant.
K_c, K_p	Equilibrium constant, when molar concentrations and partial pressures respectively are employed.
k	Velocity coefficient of reaction.
L	Latent heat per mole.
l	*Length; latent heat per gram.*
M	Molecular weight.
$M[\alpha]$	Molecular rotatory power.
$M[\omega]$	Molecular magnetic rotatory power.
m	Mass.
N	Avogadro's constant (Loschmidt's number) or number of molecules in 1 gram-molecule.
n	Refractive index.

List of Symbols, Arranged Alphabetically—(continued).

Symbol.	Name of quantity.
n_k, n_a	Transport number of kation and of anion.
n_r	Refractive index (alternative symbol).
P	Pressure.
p	Pressure.
p_c, p_r	Critical pressure : reduced pressure.
Q	Quantity of heat; quantity of electricity.
R	Gas constant per mole; electrical resistance.
R_G, R_L	Molecular refractive power, according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
r	Radius.
r_G, r_L	Specific refractive power according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
S	Entropy.
T	Absolute temperature.
T_c	Critical temperature (on the absolute scale).
T_r	Reduced temperature (absolute).
T_{cs}	Critical solution temperature (absolute).
t	Time; temperature (centigrade).
t_c	Critical temperature (centigrade).
t_{cs}	Critical solution temperature (centigrade).
t_r	Reduced temperature (centigrade).
U_k, U_a	Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm.
V	Volume.
v	Volume.
v_c, v_r	Critical volume : reduced volume.
W	*Electrical resistance (alternative symbol).*
x	Mole fraction.
a	Degree of dissociation (electrolytic, thermal, etc.); angle *of optical rotation.*
$[\alpha]$	Specific rotatory power.
γ	Surface tension; ratio of specific heats.
Δ	*Diffusion coefficient.*
δ	Variation.
∂	Partial differential.
ϵ	Electrode potential (alternative symbol); dielectric constant.
ϵ_h, ϵ_c	Electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, the potential of which is taken as zero (alternative symbols).
${}_0\epsilon_h$, ${}_0\epsilon_c$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration (alternative symbols).
η	Viscosity.
θ	Temperature (centigrade), (alternative symbol).
κ	Specific conductance (conductivity); magnetic susceptibility.
Λ	Equivalent conductivity.
Λ_{10}, Λ_v, Λ_∞	Equivalent conductivity at different dilutions (volumes in litres containing 1 gram-equivalent).
Λ_k, Λ_a	Equivalent conductivity of kation and of anion.
λ	Wave-length of light.
μ	Molecular conductivity; magnetic permeability.
π	Ratio of circumference to diameter.
Σ	Summation.
σ	Surface tension (alternative symbol).
ϕ	Fluidity.
$[\omega]$	Specific magnetic rotation.

Remarks on the Symbols Recommended by the Working Committee.

Density.—The symbol ρ was suggested by the Electrotechnical Committee of Norway. The symbol d, with the alternative symbol D to be used, for example, in the differential dD/dt, was adopted, as it is the initial letter of the name of the quantity in the different European languages, and is also most generally employed by chemists.

Volume.—The Committee adopted v, V as symbols for *volume* generally. The symbols v_a, v_m, etc., recommended provisionally by the International Commission in 1913 were omitted. In these and in other similar cases, the Committee considered that it was unwise to attempt to prescribe a definite symbol for every variation of the fundamental quantity. It was decided, therefore, to retain only the general symbol.

Pressure.—For reasons similar to those stated under "Volume," the Committee decided not to retain the symbol P for osmotic pressure.

Concentration.—A number of suggestions were received for symbols for concentration expressed in different units. The Committee, however, considered that it was not advisable at present to adopt special symbols for such quantities. The symbols c, C for concentration in general were therefore adopted, the author being left free to specify the units employed by him.

Critical Quantities.—The use of the Latin letters, recommended by the International Commission in 1913, was confirmed by the Committee. They were chosen in place of Greek letters, in accordance with a general principle adopted by the Commission that Greek characters should be used as sparingly as possible.

Viscosity.—The symbol η was recommended by the International Commission in 1913 as being in accordance with the usage among physicists. No objections to this symbol had been received, and the Committee confirmed its adoption.

Surface Tension.—The International Commission recommended the symbol γ as chief symbol for surface tension on account of its employment in the classical researches dealing with this subject. No objections to this symbol had been received, and the Committee proposed that it should be retained, along with the alternative symbol σ.

Diffusion Coefficient.—The symbol Δ was suggested by the Spanish Chemical Society; the symbol K by the Danish Chemical Society; the symbol k by the American Chemical Society; and

D by the French Chemical Society. The Committee decided to recommend the symbol Δ, which is but little used for other quantities (for example, depression of the freezing point), whereas D, K, and k are used for the important quantities, density, equilibrium constant, and velocity coefficient of reaction.

Equilibrium Constant.—The symbol K, universally employed, was retained by the Committee. The Committee adopted the suggestion, made by the Danish Chemical Society, that, where necessary or desirable, the symbols K_c and K_p be employed for the equilibrium constant when molar concentrations and partial pressures respectively are employed.

Degree of Dissociation.—The International Commission in 1913 recommended the symbol α for the degree of electrolytic dissociation in preference to the symbol γ, as the latter is employed for surface tension and for the ratio of specific heats. The Committee agreed with this, and recommended that α be adopted generally for degree of dissociation (electrolytic, thermal, etc.).

Entropy.—For this quantity, the International Commission recommended the symbol Φ, on the grounds that this symbol was used by Willard Gibbs, and also because S had been adopted for molecular heat. Objections, however, had been made to the use of Φ by the Bunsen Gesellschaft and by the Russian Physical Society, and the symbol η had been suggested by the American Chemical Society.

The Committee, after careful consideration, formed the opinion that although it is of importance to preserve, as far as possible, any symbol used in the classics of a science, reasons may exist for abandoning the classical symbol. In the present case, the symbol S appears to be most largely employed by writers on thermodynamics, and has been adopted by the International Electrotechnical Commission. For this reason, the Committee adopted the symbol S, which also has the advantage that it is a Latin and not a Greek character. The use of η as the symbol for viscosity is a further argument against the adoption of that letter as the symbol for entropy. The objection of the International Commission that S was used for molecular heat no longer exists, according to the recommendations of the Working Committee.

Specific and Molecular Heat.—On the representations of the Bunsen Gesellschaft and of the Société de chimie physique, the Committee decided to recommend the adoption of the classical symbols c and C for specific and molecular heat in place of the symbols s and S, which were recommended by the International Commission in 1913. The former symbols are those most fre-

quently employed, and have been adopted also by the Ausschuss für Einheiten und Formelgrössen.

Ratio of Specific Heats.—The International Commission in 1913 recommended the symbol γ in preference to κ as being in growing use among physicists. The Working Committee confirmed this recommendation.

Latent Heat.—The International Commission in 1913 recommended the generally employed symbols l and L for latent heat per gram and per mole (gram-molecule) respectively, the small and the capital letter being employed in accordance with general principles. The Danish Chemical Society suggested the symbol q for (reversible) latent heat, and considered that it is not necessary to have different symbols for latent heat per gram and per mole. That Society also raised objection to the use of the letters l, L on the ground that they are, or may be, employed as symbols for solubility. The Working Committee, however, confirmed the recommendation of the International Commission for the following reasons: The letter l is the initial letter of the distinctive part of the name of the quantity in the different European languages, and, further, the symbols for latent heat and solubility would occur very seldom in the same formula.

Maximum Work, or Diminution of the Free Energy of a System.—The International Commission in 1913 recommended the symbol W for "work." Whereas the Danish Chemical Society suggested that W may be used as a symbol for "work generally," objections have been raised to the use of W in the sense of "maximum work," or diminution of the free energy. Since it is the latter quantity that is of importance in physical chemistry, the Committee was of opinion that no symbol need be recommended for "work generally," and that the symbol A should be adopted for "maximum work." This symbol has been adopted by the Ausschuss für Einheiten und Formelgrössen and by the International Electrotechnical Commission, and is used in the majority of text-books and journals. The American Chemical Society recommended the symbol ψ $(= \epsilon - t\eta)$, the symbolism employed by Willard Gibbs. The Committee regretted that it felt it to be advisable, on the principle of disturbing existing usage as little as possible, not to adopt the Greek letters employed by Gibbs.

Refractive Index.—The symbol n (with n_ν as alternative) was recommended by the International Commission in 1913 as being most generally employed. The Committee confirmed this recommendation. For the specific refractive power, according to Gladstone and Dale and to Lorentz and Lorenz respectively, the symbols r_G and r_L, or, if it is desired to indicate the temperature

nd wave-length of light, the symbols $[r_a]^t_\lambda$ and $[r_L]^t_\lambda$ were adopted 3 general symbols by the Committee. The use of λ in this eneral symbol in place of D, given in the list of symbols recomıended by the International Commission in 1913, seems preferble as being more general, and because λ is the symbol for the 'ave-length of light. As a specific example, one might write $[r_a]^{18°}_D$.

Molecular Rotatory Power.—The Committee was of opinion that is more in harmony with general principles to adopt the symbol $I[a]$ for molecular rotatory power, and to redefine this as $I[a] = \frac{\text{molecular weight} \times [a]}{100} = [M]$.

Magnetic Rotation.—The Committee recommended the adoption f the symbol $[\omega]$ for specific magnetic rotation, and $M[\omega]$ for ıolecular magnetic rotatory power, which is defined in reference ɔ that of water as unit.

Resistance.—The Committee recommended the adoption of the ymbol R, which has been adopted also by the International lectrotechnical Commission. On the suggestion of the Bunsen lesellschaft, the Committee adopted the letter W as an alternative ymbol for use when confusion with the gas constant may arise.

Electrode Potential.—The International Commission in 1913 ecommended the symbol ϵ for electrode potential. Objections ave been raised to the adoption of this symbol on the grounds hat in writing, the Latin e is frequently written like the Greek ϵ, nd also that the use of ϵ, especially when the suffixes h and c, or example, ϵ_h, ϵ_c, are added, is more trying to read. As the lectrode potential is really an electromotive force, the Working ommittee was of opinion that E, the symbol for electromotive orce, may also be adopted as chief symbol for electrode potential, he symbol ϵ being, however, retained as an alternative symbol.

Dielectric Constant.—The Committee decided to adopt ϵ nstead of κ as the symbol for this quantity, as the former had een adopted by the Ausschuss für Einheiten und Formelgrössen nd by the International Electrotechnical Commission.

Equivalent Conductivity.—The adoption of the symbol Λ was onfirmed. It is defined as

$$\Lambda = \frac{1000\kappa}{\text{concentration in gram-equivalents per litre}}.$$

For the equivalent conductivity of the kation, the Committee onsidered that it is advisable to use the letter k as suffix in place f c (that is, Λ_k in place of Λ_c), since the former letter represents more correct transcription of the Greek, and is also largely used

at present. The Committee recommended that kation should always be spelt with a k.

Molecular Conductivity.—The Committee recommended the symbol μ $\left(= \frac{1000\kappa}{\text{concentration in moles per litre}}\right)$ for the molecular conductivity. This quantity was not included in the list drawn up by the International Commission in 1913. It should be noted that this symbol should not be confused with that used by W. Ostwald for the molecular conductivity measured in reciprocal Siemens units.

ALEX. FINDLAY,
Secretary to the Working Committee.

AGRICULTURAL COLLEGE AND RESEARCH INSTITUTE LIBRARY
COIMBATORE

ANNUAL GENERAL MEETING.

THURSDAY, MARCH 17TH, 1921.

Sir JAMES J. DOBBIE, D.Sc., LL.D., F.R.S., President, in the Chair.

The adoption of the Report of Council, together with the Balance Sheet and Statement of Accounts for the year ending December 31st, 1920, was proposed by Professor PYMAN and seconded by Dr. J. A. VOELCKER. The Treasurer referred to the principal items in the Accounts and answered some questions raised by Fellows. The motion was then put to the meeting and carried.

REPORT OF COUNCIL, 1920–1921.

A NET increase of 168 Fellows over that for 1918 was reported last year, and the Council is gratified to record that, notwithstanding the greater number of resignations received this year, partly owing, no doubt, to the raising of the Annual Subscription for 1921, the Society continues to grow steadily in numbers.

On December 31st, 1919, there were 3,569 Fellows. During 1920, no less than 318 Fellows were elected and 21 reinstated, *making a gross total of 3,908.* The Society *has lost* 41 *Fellows* by death; 92 resignations have been received, as against 42 in 1919; the names of 50 Fellows have been removed for non-payment of Annual Subscriptions, and the elections of 4 Fellows have been declared void. The total number of Fellows as at December 31st, 1920, *therefore,* was 3,721, *showing a net increase of* 152 Fellows over the number for the previous year.

The congratulations of the Society are offered to Major Charles Edward Beadnell, who was elected on February 7th, 1861, and has now completed his sixtieth year as a Fellow, and to the following, who have attained their jubilee as Fellows:

	Elected.
John Allen	May 5th, 1870.
Henry Edward Armstrong	Dec. 1st, 1870.
Sir James Dewar	Dec. 1st, 1870.
Richard Jackson Moss...	Jan. 19th, 1871.
Horace Tabberer Brown	Jan. 19th, 1871.
John Robert Tustin	Feb. 2nd, 1871.
William Gowland	Feb. 2nd, 1871.
Douglas Hermann	Feb. 16th, 1871.
Matthew Moncrieff Pattison Muir	Feb. 16th, 1871.
Sir Edward Thorpe	Feb. 16th, 1871.

The volume of Transactions for 1920 contains 1,648 pages, of which 1,486 pages are occupied by 182 memoirs, the remaining 162 pages being devoted to Obituary Notices, lectures on special subjects, the Report of the Annual General Meeting, the Presidential Address, and the Report of the International Committee on Atomic Weights. The volume of the preceding year contained 139 memoirs, occupying 1,392 pages. The Journal for 1920 contains also 4,074 abstracts, occupying 1,708 pages, whilst the abstracts for 1919 numbered 2,534, and occupied 1,148 pages. There has been during 1920 a very considerable increase in number of the memoirs published in journals devoted to chemistry and allied subjects, although the number is still far below that of any of the years immediately preceding the war.

The abstracts may be classified as follows:

	Pages.	No. of Abstracts.
PART I.		
Organic Chemistry	—	1362
Physiological Chemistry	—	209
Chemistry of Vegetable Physiology and Agriculture	—	330
	920	1901
PART II.		
General and Physical Chemistry	—	*1027*
Inorganic Chemistry	—	384
Mineralogical Chemistry	—	95
Analytical Chemistry	—	667
	788	2173
Totals in Parts I and II.	1708	4074

It is with profound regret that the Council has to report the sudden death, on January 31st, of Dr. Cain, who has acted as Editor of the Journal for a period of nearly fifteen years. Throughout his tenure of office he carried out his laborious duties with singular ability and devotion to the best interests of the Society, and the Council has to record its sense of the great loss the Society has sustained in his death.

For reasons of economy, it was decided to suspend for a time the publication of the monthly authors' index in the Journal, but this has now been resumed in a slightly modified form as from the January number of the Journal.

Since the last Annual General Meeting, the Society has had to mourn the loss of Professor Armand E. J. Gautier, one of its distinguished Honorary Fellows; whilst eight new Honorary Fellows have been elected, viz.: Wilder Dwight Bancroft, Victo

Grignard, Heike Kamerlingh Onnes, Emanuele Paternò, Paul Sabatier, Jean Baptiste Senderens, Sören Peter Lauritz Sörensen, and Georges Urbain.

As stated in the last Report of Council, the petition to the Privy Council for a Supplemental Charter was graciously granted by His Majesty. The necessary powers having thus been obtained, the draft Bye-Laws, on which the Council had been engaged for some considerable time, were submitted to an Extraordinary General Meeting on April 29th. With certain minor alterations, these Bye-Laws were approved by the Fellows, and came into force on June 1st, 1920. The main changes which have been effected are the admission of women to Fellowship and the alteration of the constitution of the Council to include a much larger representation of provincial Fellows. Fellows generally have now increased facilities for nominating new Members of Council, and the election of the Council in the case of a contest is carried out by means of a postal vote of Fellows resident in the United Kingdom, instead of, as formerly, at the Annual General Meeting.

In view of the fact that women have now become eligible for election as Fellows, the Council decided to abolish the class of Lady Subscribers as from December 31st, 1920.

After anxious and careful consideration of the financial position of the Society, the Council reluctantly came to the decision that it was necessary to increase the amount of the Annual Subscription. An Extraordinary General Meeting was accordingly summoned for June 24th to consider the resolutions of the Council. The matter was finally settled at a subsequent meeting held on July 20th, when the following Resolutions of Council were adopted:

(a) That the Entrance Fee be reduced from £4 to £3 as from December 1st, 1920.

(b) That the Annual Subscription to be paid by Fellows be increased from £2 to £3, beginning with the year 1921.

(c) That the Life Composition Fee, as from June 1st, 1920, be £45, and for Fellows who have paid 10 Annual Subscriptions, £30 0 0

,,	,,	,,	15	,,	,,	22	10	0
,,	,,	,,	20	,,	,,	18	0	0
,,	,,	,,	25	,,	,,	15	0	0

The Council is gratified to find that the special lectures, which are being given this year in the Hall of the Institution of Mechanical Engineers, continue to meet with the appreciation of Fellows, and that the attendance at the Ordinary Scientific Meetings has very considerably increased.

On October 28th Dr. M. O. Forster delivered the Emil Fischer

Memorial Lecture—since issued in separate form—and this was followed on December 16th by a lecture entitled "Some Properties of Explosives," by Sir Robert Robertson. The next lecture is to be given on April 7th by Dr. F. W. Aston, who has chosen as his subject "Mass Spectra and Atomic Weights," whilst the Hugo Müller Lecture, entitled "The Natural Photosynthetic Processes on Land and in Sea and Air, and their Relation to the Origin and Preservation of Life upon the Earth," will be given by Prof. Benjamin Moore on June 16th.

The Council desires to record its thanks to those Fellows who have contributed to Volume XVII. of the Annual Reports, and also to the Abstractors for their valuable services during the past year.

A proposal has been received from the American Chemical Society suggesting co-operation in securing a wider circnlation of the Annual Reports amongst members of that Society, and the Council has agreed that the Annual Reports for 1920 should be offered to Members of the American Chemical Society at 7*s.* per copy, post free.

Permission has been granted to Dr. H. Kling to publish a French translation of the Annual Reports for 1919.

In connexion with the Tables of Physico-Chemical Symbols, referred to in last year's Report, the Council, after securing the approval of the Union Internationale de la Chimie Pure et Appliquée, has arranged for the publication of the Tables at an early date.

In response to various representations, the Council summoned a Conference last July to consider a number of matters connected with laboratory construction and equipment. The questions more especially considered were whether, in view of present costs, economies could be effected, and whether it were possible or desirable to institute organised research aiming at the utilisation of cheaper, yet sufficiently resistant, materials. The Conference reported that, as a first step, fuller details as to present practice and experience were required, and the Council accordingly appointed a Committee, consisting of Dr. C. A. Keane, Prof. J. C. Philip, and Dr. Alexander Scott, to collect the desired information. A grant has been made from the Research Fund to cover the cost of the Committee's work, and it is hoped that a report will shortly be prepared for submission to the Council and Conference.

In consequence of a communication received from the Conjoint Board of Scientific Societies regarding the position of scientific men and institutions in Austria, the Council decided to present

the current Journal to five of the prominent Universities and Technical High Schools in that country. The Journal has also been presented to the University at Zagreb.

The question of approaching the Government with regard to a grant in aid of Scientific Societies was raised by the Conjoint Board of Scientific Societies. The Council informed the Board that whilst it would support such applications by other Societies which were in need of financial assistance, it did not propose at present to apply on behalf of the Chemical Society. The Board was urged to impress upon the Government the need for a reduction in the postal rates for scientific publications.

As a result of the appeal made by the President for contributions towards a fund to provide for the erection of a Gerhardt monument in Strasbourg, the sum of £213 12*s.* 6*d.* was received, and, in addition to this, several contributions from Fellows were sent direct.

In response to a communication from the National Physical Laboratory, a Committee, consisting of Prof. A. J. Allmand, Mr. J. L. Baker, Mr. F. H. Carr, and Dr. B. Dyer, was appointed to consider the testing of graduated glassware. The Committee reported that generally there is no ground for dissatisfaction with the existing regulations and tolerances as a recognised standard for apparatus of commercial quality, but recommended the use of the Mohr system instead of the present principle adopted for graduation. The report was accepted and communicated to the Director of the National Physical Laboratory.

Reference was made in the last Report of Council to the position selected for the Harrison Memorial. It has been decided to set aside the whole of the alcove in the wall on the first landing for the memorial, with which will be combined an appropriate tablet bearing the names of the other Fellows of the Society who died on service. The artist is now actively engaged on the work, and it is hoped that it may be possible to erect the memorial during the current year.

The Federal Council has presented a memorandum on co-operation between the Society of Chemical Industry and this Society in the publication of chemical literature. It is suggested that greater economy and efficiency could be obtained if the two Societies were amalgamated into a "Chemical Federation" for purposes of publication. The important questions raised by the memorandum are now under consideration by a joint committee composed of the following: Sir William Pope, Mr. E. V. Evans, Dr. C. A. Keane, Dr. Miall, as representing the Society of Chemical Industry, and Dr. M. O. Forster, Mr. A. J. Greenaway,

Prof. J. C. Philip, and Prof. W. P. Wynne as representing the Chemical Society.

Prof. H. E. Armstrong, Sir William Pope, and Prof. J. C. Philip were appointed as representatives of the Society on the Federal Council for Pure and Applied Chemistry for 1921, whilst Dr. Alexander Scott and Prof. Samuel Smiles agreed to act as delegates of the Society on the Conjoint Board of Scientific Societies for 1921.

The Council has nominated Mr. F. H. Carr to represent the Society on the Sectional Committee on Chemical Engineering of the British Engineering Standards Association.

In connexion with the supply of scientific glassware and fine chemicals, the Council has adopted the view that it is desirable to prohibit importation for a limited time except under licence, but that the granting of such licences should be under the control of a Committee composed in such a way as to secure fully the interests of the users. The views of the Council on these matters have been made known to the Board of Trade, both by letter and by deputation.

In November, 1917, a Committee was appointed to consider and report on the constitution of the International Atomic Weights Committee. Acting on the recommendation of this Committee, the Council is supporting the proposal that the names of Profs. T. W. Richards, P. A. Guye, B. Brauner, and R. Nasini should be added to the present International Committee. The views of the Council will be submitted to the Inter-Allied Conference at Brussels in March, 1921. Sir Edward Thorpe has been appointed by the Chemical Society on the International Committee.

The complete scheme for the extended use of the Library has now been in operation since May, 1919, and there is abundant evidence that the extra facilities for using the Library are appreciated. During the additional hours in which the Library is now open, 1,550 attendances were recorded in 1920, as against 1,198 in 1919.

The cost incurred in 1920 in connexion with the scheme amounted to some £590, and towards this sum donations amounting to £411 5s. 0d. have been received from the contributing Societies. This shows a deficit of about £178, and it is considered that, owing to the increased use of the Library by our own Fellows the sum of £110 as salary of the junior assistant, who was originally employed on account of the increased hours involved in the scheme, should now be charged to the Society. It is estimated that the sum of £600 will be required to continue the scheme

during 1921, and communications have been addressed to the contributing Societies asking for at least as hearty support as has been afforded in the past.

The books borrowed from the Library during 1920 numbered 3,079, as compared with 2,867 in 1919. The additions to the Library comprise 312 books, 439 volumes of periodicals, and 196 pamphlets, and show increases over the previous year of 123, 184, and 110 respectively.

As anticipated at the last Annual General Meeting, the accounts for the year 1920 show, for the first time since 1913, a deficit on the year's working. This amounts to £1,310 6*s.* 7*d.*, because the expenditure, having increased by £3,730 15*s.* 10*d.*, has reached £15,046 14*s.* 2*d.*, whilst the income is greater by £1,898 6*s.* 0*d.* only, and aggregates £13,736 7*s.* 7*d.* By comparison with the previous year, however, the position is even more unfavourable than that suggested by the above deficit, because that year showed a balance of income over expenditure amounting to £522 3*s.* 3*d.*; moreover, the life composition fees received in 1920 have amounted to £931 10*s.* 0*d.* in excess of this item for 1919, and thus the real deficit as compared with the working of that year is £2,763 19*s.* 10*d.*

Besides the source already mentioned, increase of revenue arises from annual subscriptions, £293 10*s.* 0*d.*, interest on investments, £99 13*s.* 10*d.*, sale of publications, £353 6*s.* 8*d.*, and donations to the Library, £271. The increase of £3,730 15*s.* 10*d.* in expenditure is £8 8*s.* 1*d.* more than the corresponding increase shown by 1919 over 1918, and the aggregate of £15,046 14*s.* 2*d.* has sprung from £7,593 10*s.* 7*d.* since December 31st, 1918. Thus the expenditure of the Society has approximately doubled itself in two years.

Once more the cost of publications is responsible for a large proportion of this increase, namely, £2,171 0*s.* 5*d.*; although this is due principally to increased cost of printing the Journal, namely, £1,340 9*s.* 4*d.*, the editorial salaries have been increased by £265 and fees to abstractors by £356 12*s.* 5*d.*, the rate of payment being now twice that prevailing before the war. Library expenses show an increase of £403 11*s.* 9*d.*, and administration an increase of £1,004 8*s.* 11*d.*, made up of staff salaries increased by £168 8*s.* 6*d.*, war bonus (including editorial) by £176 15*s.* 7*d.*, stationery by £139 2*s.* 9*d.*, and postages by £75 9*s.* 0*d.*; the largest contribution, however, is on account of the Supplemental Charter and new Bye-Laws, legal expenses amounting to £261 5*s.* 0*d.*, whilst a portion of the miscellaneous printing, increased by £105 9*s.* 3*d.*, is due to the same cause.

The Journal has continued to expand, the major increase during the past year being due to the abstracts :

	Number of Pages.		
	Trans.	Abstr.	Total.
1914	2,909	2,068	4,977
1915	1,862	1,944	3,806
1916	1,368	1,532	2,900
1917	1,128	1,308	2,436
1918	995	1,032	2,027
1919	1,517	1,148	2,665
1920	1,648	1,708	3,356

The Council is gratified to note the response made by authors to its appeal for economy; although the number of original papers increased from 139 to 182, the proportion of pages occupied was much smaller. The Council believes that more might be accomplished in this direction without impairing the value of authors' communications, and the need for such economy is even more urgent, because the cost of the Journal per page was £2 9*s*. 3*d*. for 1920, as against £2 4*s*. 8*d*. for 1919 and 17*s*. 9*d*. for 1914. At various times during the past five years ten separate demands have been made for an increase in printing charges, which now represent 2¼ times those levied in 1915.

Early in the year under review, expert advice was taken regarding the quality and cost of the paper used for the Journal, and an independent examination of the printing charges was made, but in neither case was there ground for believing that economy could be effected during the conditions now prevailing. Thus there seemed no alternative to the step recommended by the Council and adopted by the Society in July, namely, raising the subscription from £2 to £3 as from January 1st, 1921. The price of the Journal to the public has been increased from £3 to £4.

Owing to the debit balance, further investments have not been made, but a legacy of £1,000 having been received under the will of the late Dr. Rudolph Messel, it has not been necessary to realise any securities to meet the deficit; meanwhile the market value of the Society's investments shows a further decline of £1,133 7*s*. 7*d*.

The following grants have been made from the Research Fund during the year :

Measurement of the effect of hydroxy-acids on the rate of hydrolysis of methyl acetate. F. L. Allen	£10	0	0
New derivatives of the hexoses. C. F. Allpress	10	0	0
Esters and organic salts of cobalticyanic acid. F. Arnall	10	0	0
(*a*) Anthracene derivatives, (*b*) Phthaloylacenaphthene, (*c*) Action of nitric acid on thiocarbamides. E. de B. Barnett	15	0	0

Oximino-derivatives (continued). O. L. Brady	£5	0	0
The biochemistry of iodine (continued). A. T. Cameron ...	15	0	0
Organo-derivatives of bismuth (continued). F. Challenger	6	0	0
Bridged homocyclic rings in relation to their homocyclic unsaturated isomerides. J. P. C. Chandrasena ...	10	0	0
The preparation of alkylene sulphonates and sulphonic chlorides. J. B. Cohen	2	0	0
Morphological studies of benzene derivatives. R. T. Colgate	10	0	0
Derivatives of pyrone and benzopyrone. S. S. Deshapande	10	0	0
A new method of halogenation. S. N. Dhar	20	0	0
Action of diazo-salts on aromatic sulphonamides. P. K. Dutt	5	0	0
Reduction of aromatic nitro-compounds. P. K. Dutt ...	5	0	0
Melting points of homologous series. W. E. Garner ...	15	0	0
Constitution of acids and their salts (continued). J. C. Ghosh	10	0	0
Attempt to synthesise curcumin. P. C. Ghosh	20	0	0
Organo-metallic compounds of thallium and cadmium. A. E. Goddard	10	0	0
Synthesis of hydroxy-*o*-ketonic acids. G. Greenwood ...	5	0	0
Influence of negative groups on the reactivity of the methylene group. B. M. Gupta	10	0	0
Action of bromine on phenanthrene (continued). H. Henstock	10	0	0
Studies in the hydroaromatic series. L. E. Hinkel ...	8	0	0
Determination of vapour pressures of hydrated salts and of copper nitroxyl and other salts. D. B. Huntingford ...	20	0	0
Formation and structure of unsaturated compounds, etc. C. K. Ingold	30	0	0
Polycyclic compounds in relation to their homocyclic unsaturated isomerides. F. W. Jeavons	10	0	0
Influence of nitro-groups on the reactivity of substituents in the benzene nucleus (continued). J. Kenner	5	0	0
Reactions of diethyl acetonedicarboxylate. J. Kenner ...	10	0	0
Compounds of phenolphthalein. S. Krishna	10	0	0
Constitution of amygdalin. Miss G. C. Leitch	10	0	0
The theory of colloids. J. W. McBain	40	0	0
Researches on diazophenols (continued). G. T. Morgan ...	7	0	0
Catalytic hydrogenation. W. W. Myddleton	20	0	0
The reactivity of sulphur chloride (continued). K. G. Naik	10	0	0
Synthesis of *iso*butenetricarboxylic acid. L. C. Nickolls ...	10	0	0
Constitution of catechin. M. Nierenstein	15	0	0
Preparation of tetracarboxylic acid. K. C. Pandya ...	10	0	0
The study of *m*-nitro-amines and *m*-diamines of *m*-xylene. S. A. Pearman	10	0	0
(*a*) *The constitution of santal and santalone*, (*b*) *Syntheses* by means of quercetin. A. G. Perkin	20	0	0
Synthesis of *iso*butenetricarboxylic acid. W. J. Powell ...	10	0	0
Effects of impurities on the catalytic oxidation of ammonia. A. W. Pritchard	15	0	0
The constitution of the metallic derivatives of alkaloids, acid amides, thio-acid amides, and other substituted acid amides. J. N. Rakshit	5	0	0
Constitution of galacto-arabinose. W. G. Sedgwick ...	10	0	0

Relation of polycyclic compounds to their homocyclic unsaturated isomerides. E. A. Seeley	£10 0 0
Reduction of ω-nitrostyrene and some of its derivatives. H. Stephen	10 0 0
The effect of cathode rays on certain substances. F. W. Turner	20 0 0
Oxidising properties of sulphur dioxide. W. Wardlaw ...	10 0 0
Reaction of *d*- and *l*-α-bromo-*n*-butyric acids. E. J. Williams	10 0 0
Total ...	£558 0 0

The aggregate exceeds by £200 the sum of the payments made in 1919; hence the balance of income over expenditure is only £123 1*s.* 4*d.* as against £349 13*s.* 11*d.* for 1919. The return from investments was £50 0*s.* 10*d.* higher, and repayment of grants amounted to £32 13*s.* 1*d.* more, but the proceeds from selling platinum and gold did not recur.

The vote of thanks to the Auditors for auditing the Accounts for the past year proposed by the Treasurer, seconded by Mr. JOHN HUGHES, was carried unanimously, Dr. SENTER making acknowledgment.

Dr. J. I. O. MASSON proposed a vote of thanks to the Treasurer, Secretaries, and Council for their services during the past year. This was seconded by Dr. T. SLATER PRICE and acknowledged by Mr. JULIAN L. BAKER, retiring member of Council.

The President announced that the votes recorded for the election of Fellows to vacancies on the Council resulted as follows:

A. Ordinary Members of Council resident within fifty miles of Charing Cross:

T. Slater Price (381).
J. S. S. Brame (352).
E. V. Evans (347).
O. L. Brady (164).
B. Campbell (105).

B. Ordinary Members of Council resident beyond fifty miles from Charing Cross:

C. H. Desch (409).
R. Robinson (386).
W. Rintoul (377).
H. B. Hartley (375).
N. V. Sidgwick (317).
T. S. Patterson (284).
D. R. Boyd (196).
I. M. Heilbron (157).
J. Reilly (109).

The names of the Fellows elected to vacancies on the Council were then read as follows:

President.—Sir James Walker, D.Sc., LL.D., F.R.S.

Vice-Presidents who have filled the office of President.—Henry Edward Armstrong, Ph.D., LL.D., F.R.S.; Sir James Johnston

Dobbie, M.A., D.Sc., F.R.S.; William Henry Perkin, Sc.D., D.Sc., F.R.S.; Sir William Jackson Pope, K.B.E., M.A., D.Sc., F.R.S.; Alexander Scott, M.A., D.Sc., F.R.S.; Sir William Augustus Tilden, D.Sc., F.R.S.

Vice-Presidents who have not filled the office of President.—Frederick Gowland Hopkins, M.A., D.Sc., F.R.S.; Frederic Stanley Kipping, D.Sc., F.R.S.; Jocelyn Field Thorpe, C.B.E., D.Sc., F.R.S.

Ordinary Members of Council.—John Samuel Strafford Brame; Cecil Henry Desch, D.Sc., Ph.D.; Edward Victor Evans, O.B.E.; Harold Brewer Hartley, M.A., C.B.E.; Thomas Stewart Patterson, D.Sc., Ph.D.; Thomas Slater Price, O.B.E., D.Sc., Ph.D.; William Rintoul, O.B.E.; Robert Robinson, D.Sc., F.R.S.; Nevil Vincent Sidgwick, M.A., Sc.D.

Messrs. R. C. Farmer, G. Senter, and C. K. Tinkler were elected Auditors for the current financial year.

The meeting then proceeded to consider two proposals (received by the Council in writing and signed by twenty Fellows) for the alteration of Bye-law XVI. The first proposal was that for the words:

> "The Society shall have the right to retain the manuscript and illustrative drawings of all papers sent to the Society."

there be substituted the words:

> "The manuscript and illustrative drawings of any paper considered by the Council unsuitable for publication shall be returned to the author immediately on his demand."

This motion having been formally proposed and seconded, the President read the Council's report recommending the rejection of the proposal. Thereafter Prof. J. C. Philip spoke to this report, directing attention to the permissive character of the clause in its present form, and pointing out that in this way opportunity was given for the treatment of each case on fair and reasonable lines. The desirability, however, of preserving in certain cases, for purposes of record, the original paper as communicated to the Society was emphasised, and it was further pointed out that in those cases where a paper was not accepted for publication in the Journal the author was at perfect liberty to publish elsewhere. After remarks by the Treasurer and a number of other Fellows, the motion was put to the meeting and lost, no votes being recorded in its favour.

INCOME AND EXPENDITURE ACCOUNT

Income.

	£	s.	d.	£	s.	d.
To Life Compositions ...				1543	10	0
,, Admission Fees ...				1104	0	0
,, Annual Subscriptions—						
Received in advance, on account of 1920 ...	418	0	0			
,, during 1920 ,, ,, ...	5277	0	0			
,, ,, ,, ,, 1919 ...	246	0	0			
,, ,, ,, ,, 1918 and previous years ...	56	0	0			
	5997	0	0			
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet ...	270	0	0			
	5727	0	0			
Add Arrears at date: 1920, £328; 1919 and previous Years, £10. Estimated to realise as per Balance Sheet ...	260	0	0			
				5987	0	0
,, Lady Subscribers ...				13	10	0
,, *Investments*:—						
Dividends on £6730 Metropolitan Consolidated 3½ per cent. Stock	235	11	0			
,, £1050 London and North Western Railway 3 per cent. Debenture Stock ...	22	1	0			
,, £1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock ...	31	18	8			
,, £1400 India 2½ per cent. Stock ...	35	0	0			
,, £2400 Bristol Corporation 2½ per cent. Debenture Stock	42	0	0			
,, £4341 Midland Railway 2½ per cent. Preference Stock	75	19	4			
,, £1200 Leeds Corporation 3 per cent. Stock ...	25	4	0			
,, £1500 Transvaal 3 per cent. Guaranteed, 1923/53 ...	45	0	0			
,, £1200 North British Railway 3 per cent. Debenture Stock ...	25	4	0			
,, £700 Canada 3½ per cent. 1930/50 ...	19	12	0			
,, £2100 5 per cent. War Stock ...	105	0	0			
,, £1100 5 per cent. War Bonds ...	38	10	0			
,, £2000 5 per cent. National War Bonds, 1927 ...	100	0	0			
,, £2000 5 per cent. National War Bonds, 1928 ...	100	0	0			
,, £600 Funding Loan, 4 per cent., 1960–90 ...	16	16	0			
,, Income Tax Recovered ...	174	10	4			
,, Interest on Deposit ...	26	10	11			
				1118	17	3
,, Publication Sales:—						
Journals ...	2320	16	7			
Proceedings ...	21	18	6			
Collective Index...	93	18	6			
Library Catalogue ...	0	4	6			
Atomic Weight Tables ...	2	7	2			
Jubilee Volume ...	0	10	0			
Annual Reports on Progress of Chemistry ...	368	13	7			
Memorial Lectures (including Fischer Lecture) ...	19	0	3			
Gummed Abstracts ...	34	10	0			
	2861	19	1			
Less Publishers' Commission ...	270	5	0			
				2591	14	1
,, Proceeds of Advertisements in Journal ...	991	2	8			
Less Commission ...	68	11	7			
				922	11	1
,, Miscellaneous Receipts ...				21	9	2
,, Donations to Library ...				411	15	0
,, Subscriptions from other Societies ...				22	1	0
				13736	7	7
,, Balance being Excess of Expenditure over Income, carried to Balance Sheet ...				1310	6	7
				£15,046	14	2

FOR THE YEAR ENDED 31ST DECEMBER, 1920.

Expenditure.

	£	s.	d.	£	s.	d.
By Expenses on account of Journal:—						
Salary of Editor, including Indexing	800	0	0			
Salary of Sub-Editor and Assistant	335	0	0			
Editorial Postages	36	10	9			
Abstractors' Fees	750	2	3			
Printing of Journal	5965	11	11			
Banding	143	14	0			
Printing of Advertisements	324	2	3			
Wrappers and Addressing	10	18	5			
Distribution of Journal	763	12	7			
Authors' Copies	268	0	4			
Insurance of Stock	14	11	7			
				9412	4	1
,, Meetings, Hire of Hall, etc.				32	1	4
,, Annual Reports on the Progress of Chemistry				626	15	10
,, Purchase of Back Numbers of Journal				12	8	11
,, List of Fellows, Printing, etc.				166	13	11
,, Charter and Bye-Laws, Printing, etc.				56	11	5
,, Library Expenses:—						
Salaries	752	16	6			
Books and Periodicals	495	12	1			
Binding	104	19	4			
				1353	7	11
,, Indexing for International Catalogue				30	0	0
,, Advertisements of Meetings				12	19	6
,, Donations:—						
Federal Council for Pure and Applied Chemistry	113	10	0			
Conjoint Board of Scientific Societies	5	5	0			
				118	15	0
,, Administrative Expenses:—						
Salary of Staff	854	0	0			
War Bonus	612	2	6			
Wages (Commissionaire, Housekeeper, and Charwoman)	299	2	9			
Coal and Lighting	92	8	1			
House Expenses and Repairs	102	14	2			
Telephone	18	0	0			
Furniture	60	9	3			
Tea Expenses	66	14	1			
Insurances	17	7	1			
Accountants' Charges	21	0	0			
Commission on Recovery of Income Tax	8	14	6			
Law Costs (Supplemental Charter and New Bye-Laws)	261	5	0			
Miscellaneous Printing	282	9	4			
Stationery	296	12	7			
Postages	197	13	1			
Miscellaneous Expense	34	3	10			
				3224	16	3
				£15,046	14	2

THE CHEMICAL SOCIETY.—BALANCE SHEET, 31st December, 1920.

Liabilities.

		£	s.	d.	£	s.	d.
To Subscriptions received in advance... ...	For 1921	688	14	0			
	For 1922	9	0	0			
					697	14	0
,, Sundry Creditors					2117	3	4
,, Bank—Current Account Overdrawn					200	8	5
,, Research Fund:—							
As per last Account		15246	11	0			
Add Excess of Income over Expenditure for the year		123	1	4			
					15369	12	4
Chemical Society:—							
Excess of Assets over Liabilities as per last Balance Sheet...		27769	15	0			
Deduct Excess of Expenditure over Income for the Year		1310	6	7			
		26459	8	5			
Add Legacy received during the Year		1000	0	0			
					27459	8	5
					£45844	6	6

Assets.

	£	s.	d.	£	s.	d.
By Investments (value when acquired):—						
£6730 Metropolitan Consd. 3½ per cent. Stock A	7212	8	6			
£1050 *London and North Western* Railway 3 per cent. Debenture Stock	839	12	0			
£1520 14*s*. 5*d*. Cardiff Corporation 3 per cent. Stock	1650	0	0			
£1400 India 2½ per cent. Stock	1316	1	0			
£2400 *Bristol* Corporation 2½ per cent. Debenture Stock	2070	2	0			
£4341 Midland Railway 2½ per cent. Preference Stock	3572	2	5			
£1200 Leeds Corporation 3 per cent. Stock	1143	1	0			
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	1460	13	6			
£1200 *North British* Railway 3 per cent. Debenture Stock	1033	11	0			
£700 Canada 3½ per cent. Stock, 1930/50	704	8	6			
£2100 5 per cent. War Stock, 1929/47	1995	0	0			
£1100 5 per cent. National War Bonds 1929/47 ...	1045	0	2			
£2000 *Registered 5 per cent. National War Bonds* 1927	2000	0	0			
£2000 Registered 5 per cent. National War Bonds 1928	2000	0	0			
£600 4 per cent. Funding Loan, 1960/90...	480	0	0			
(Market Value £19,404 17*s*. 8*d*.)				28522	0	1
,, Sundry Debtors				1624	5	8
,, Subscriptions in Arrear £338. Estimated to realise				260	0	0
,, Insurance paid in advance				36	19	6
,, Cash in hand				31	8	11
,, Research Fund:—						
Investments (value when acquired):						
£1000 North British Railway 4 per cent. No. 1 Preference Stock	1010	0	0			
£4400 Metropolitan Consolidated 3½ per cent. Stock "B" Account	4587	18	0			
£1034 Great Western Railway 2½ per cent. Debentures	1049	15	11			
£1142 16*s*. 0*d*. New South Wales 3 per cent. Stock ...	1000	0	0			
£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002	16	9			
£1365 Midland Railway 2½ per cent. Debenture Stock	1010	0	9			
£806 Victoria 3 per cent. Stock	706	6	2			
£4498 11*s*. 0*d*. 5 per cent. War Stock...	4267	4	10			
£300 *National War Bonds 1928. 3rd Series*	300	0	0			
				14934	2	5
(Market Value £10,854 14*s*. 2*d*.)						
,, Cash at Bank				435	9	11
				£45844	6	6

I have examined the above Balance Sheet and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

ARTHUR R. LING,

Research Fund Income and Expenditure Account for the Year ended 31st December, 1920.

Income.	£	s.	d.	£	s.	d.
To Dividends on :—						
£1000 North British Railway 4 per cent. No. 1 Preference Stock	28	0	0			
£4400 Metropolitan Consolidated 3½ per cent. Stock ...	154	0	0			
£1034 Great Western Railway 2½ per cent. Debenture Stock	18	1	10			
£1142 16s. New South Wales 3 per cent. Debenture Stock	34	5	8			
£1122 Metropolitan Water Board 3 per cent. "B" Stock	28	12	3			
£1965 Midland Railway 2½ per cent. Debenture Stock	23	17	9			
£806 Victoria 3 per cent. Stock	16	18	6			
£4498 11s. 0d. 5 per cent. War Loan, 1929–47	224	18	6			
£300 5 per cent. National War Bonds, 1928	15	0	0			
				543	14	6
,, Income Tax Recovered				87	2	8
,, Repayment of Grants				69	8	8
				£700	5	10

Expenditure.	£	s.	d.
By Grants	558	0	0
,, Travelling Expenses	9	15	4
,, Commission on Recovery of Income Tax	4	7	2
,, Advertisements	4	6	0
,, Cheque Book	0	16	0
,, Balance, being excess of Income over Expenditure, carried to Balance Sheet	123	1	4
	£700	5	10

The second proposal, that the passage

> "It shall consist of such of the papers which have been communicated to the Society, or of abstracts of them, as the Council may determine"

be altered by deleting the words

> ", or of abstracts of them,"

was then considered. The adverse report of the Council on this proposal was read, and in reply to a point raised by Dr. BRADY, Prof. PHILIP made a statement on the practice adopted in connexion with the publication of papers. While the Council, on financial and other grounds, regarded as essential the power to require an author to shorten his paper before publication, it was made clear that if the author objected to such publication in an abbreviated form the paper could be withdrawn and the author was then at liberty to offer it elsewhere for publication. The motion was put to the meeting and lost, no votes being recorded in its favour.

In presenting the Longstaff Medal to Prof. Jocelyn Field Thorpe, C.B.E., F.R.S., the PRESIDENT referred to Prof. Thorpe's important and numerous contributions to Organic Chemistry, and said that "all these inquiries, in carrying out which he had aroused the enthusiastic co-operation of numerous younger collaborators, have been marked by conspicuous experimental skill and admirable theoretical insight." The award was acknowledged by Prof. THORPE in appropriate terms.

The PRESIDENT then delivered his address, entitled, "The Study of the History of Chemistry; its Importance and Uses."

A vote of thanks to the President for his services in the Chair during the past two years and for his address, coupled with the request that he would allow the address to be printed in the Transactions, was proposed by Prof. A. SMITHELLS, C.M.G., F.R.S., seconded by Prof. J. M. THOMSON, and carried with acclamation, the PRESIDENT making acknowledgment.

OBITUARY NOTICES.

SIR WILLIAM DE WIVELESLIE ABNEY, K.C.B., D.C.L., D.Sc., F.R.S., etc.

BORN 1843; DIED DECEMBER 2ND, 1920.

SIR WILLIAM ABNEY was a man of many activities. In 1861 he became a lieutenant in the Royal Engineers, and in 1872 we find him described as "Assistant Instructor in Telegraphy" at the School of Military Engineering, Chatham. Later in the year (1872) he was appointed "Instructor in Chemistry and Photography" at the same school for the usual period of five years. He was made Captain in 1873, and in 1877 he left Chatham and became connected with the Science and Art Department as a Science Inspector. While at Chatham he had formed a very definite opinion that instruction in science should be imparted not merely by lectures, books, and cram work, but by means of practical work on the part of the student. So he devoted himself to the drawing up of specifications of laboratory accommodation and equipment that could be recognised as suitable, for at that time there were not half-a-dozen laboratories connected with the Department that were worthy of the name. In 1881 he retired from the army, and seven years after he had become associated with the Science and Art Department (1884) the half-a-dozen recognised laboratories had increased to more than 100, and he was appointed "Director for Science." This work rapidly progressed under his superintendence, and in 1903 we find that there were 349 physical and 774 chemical laboratories, besides laboratories for mechanics, metallurgy, and biology, working in connexion with the Science and Art Department. In 1899 Sir William was appointed "Principal Assistant Secretary of the Board of Education, South Kensington," that is, the chief officer of the science division of the Board. The changes consequent on the passing of Mr. Balfour's Education Act of 1903 led to his retirement. From that time he was "Adviser to the Board of Education (Science Department)," and a "Member of the Advisory Council for Education" to the War Office.

Although his life was so fully occupied with official duties, Abney found time to carry ont a very large amount of scientific work. In 1862, at the age of nineteen, he began to study photography, and in 1870 he joined the Photographic Society of London (now the Royal Photographic Society). In 1871 he became a Fellow of the Chemical and of the Royal Astronomical Societies, and in

1876 he was elected a Fellow of the Royal Society, and a member of the Physical Society of London. He was no sleeping member of the societies to which he belonged; he took an active part in the management of some of them and contributed largely to their proceedings. He was elected President of the Royal Photographic Society, 1892—1894, 1896, and 1903—1905; President of the Royal Astronomical Society, 1893—1895; and of the Physical Society, 1895—1897. In 1889 he was President of the Mathematical and Physical Section of the British Association (Newcastle-upon-Tyne); in 1903 President of the Educational Science Section of the British Association (Southport); in 1904 Chairman of the Royal Society of Arts; and he was President of the original Camera Club during the whole of its life.

Abney said, in 1903, that "the work of the late Science and Art Department was largely a missionary work," and he himself was an enthusiastic evangelist. He was content neither with seeking the truth nor even with finding it, but was always endeavouring to get others to join in the search and to spread abroad a sound scientific knowledge. He contributed innumerable papers to periodicals and gave many lectures before all sorts of institutions, including three courses of Cantor Lectures before the Royal Society of Arts. The chief of his books, for he published a great many, generally small volumes, are "Instruction in Photography" (1872), which has grown very considerably in size during its eleven editions, his "Treatise on Photography" (1878), "Thebes and its Five Great Temples" (1876), "Pioneers of the Alps," of which he was joint author (1888), "Colour Measurement and Mixture" (1891), and the "Trichromatic Theory of Colour" (1914). He gave the Bakerian Lecture before the Royal Society in 1880 and in 1886. In 1883 the Royal Society awarded him the "Rumford" medal for his researches in Spectrum Analysis, and he was twice awarded the Progress Medal of the Royal Photographic Society (1878, 1890).

With regard to Abney's scientific work, this is not the place to refer in detail to his photographic, astronomical, and physical investigations, neither to his researches into the physics and physiology of colour vision. In these subjects he did a great deal of genuine pioneer work. Chemistry, as such, was apparently not to his taste, but occasionally he crossed the boundary, and when he did so he, as was his habit, did not leave the matter until he had done something noteworthy.

In 1872, that is, the year in which he was appointed Instructor in Chemistry and Photography at Chatham, he communicated to the Photographic Society a "Note on Silicates of Silver." He prepared two, of which he determined the formulæ by analysis.

$AgOSiO_2 + 2HO$ (old atomic weights), prepared by adding excess of silver nitrate to a sodium silicate solution, is yellow and becomes purple by exposure to light. $AgO2SiO_2 + 2HO$ is prepared by adding excess of sodium silicate to silver nitrate solution, and is white, and becomes brown or nearly black by exposure to light. Both compounds will give a developable as well as a printed-out image and both are soluble in sodium thiosulphate and potassium cyanide. He describes their uses in emulsion making, but I have not found any further reference to them.

The work for which chemists are especially indebted to Abney concerns the infra-red of the spectrum. It was in 1874 that he definitely set himself the task of photographing this region, a bold resolution to make, seeing that there was nothing known that was suitably sensitive to the infra-red. We may note that Vogel, a few months before, had discovered the colour-sensitising action of certain dyes and photographed to a little beyond A, and about 1840 Dr. John William Draper, of New York University, had gone rather further into the infra-red, using daguerreotype plates, but the image he got in the red and infra-red was reversed, that is, this region by their method undid the normal photographic action. Sir John Herschell and Robert Hunt had examined a great variety of substances with regard to their general sensitiveness to light, including the red end of the spectrum.

Abney had, therefore, first to get a suitably sensitive substance. He was very faithful to his theories and they served him well, for after long and tedious experimenting in the direction they indicated he was able to produce with certainty a collodion emulsion sensitive to the whole spectrum from the ultra-violet to a wave-length of 2200 $\mu\mu$ in the extreme infra-red, that is, a spectrum about six times as long as the visible part in a normal spectrum. With this means of investigation, he mapped the solar spectrum from wave-length 715 $\mu\mu$ to 1000 $\mu\mu$, or a little beyond, that is as far as it extends. He also found that with the exception of sodium and calcium no metallic vapours seem to give lines in the infra-red. In conjunction with General Festing, he mapped the infra-red absorption spectra of about fifty organic compounds and six inorganic liquids. From these results the lines due to hydrogen were identified, and also the bands due to several organic radicles. These results were communicated to the Royal Society (1880 to 1886).

Abney made one communication to the Chemical Society, namely, a lecture on "Colour-photometry," which he delivered in 1891. He demonstrated that any colour can be exactly described (so far as visibility is concerned) by three numbers, which will serve at

any future time for its exact visual reproduction. These numbers represent (1) luminosity; (2) hue (a wave-length, or in the case of purple the wave-length of the complementary hue); and (3) purity (or freedom from white light). He pleads with chemists to be more exact in their description of colours.

Regarding Abney as a man, he was eminently just, sincerely kind, and hated snobbishness in any form. He was a man of vast energy and indomitable perseverance. For many years he suffered much with rheumatic complaints, especially in the region of one hip, and this eventually made him lame. In spite of his suffering he was reluctant to give up his work, and the last few times that he went to the Imperial College he had to be carried from his motor-car upstairs to his laboratory.

C. J.

HENRY BASSETT, F.I.C.

BORN 1837; DIED AUGUST 30TH, 1920.

HENRY BASSETT, who died on August 30th, 1920, at the age of eighty-three, had been a Fellow of the Society since 1864, and many of our older Fellows, besides those who enjoyed his friendship, will remember him as a once-constant attendant at its meetings and as a member of its Council, on which he served for two full periods, 1870—1873, and 1890—1893.

He received his early chemical training from Hofmann in the old College of Chemistry, whence he went to Oxford for a time as assistant to Sir Benjamin Brodie. He returned to London and established himself in a little laboratory (which he called "The Den") in the Polygon, Somers Town, migrating afterwards to Euston Grove (remembered as "Den No. 2"), where he worked and experimented for several years. A good portrait of him by Houghton, painted in the Euston Grove "Den" and exhibited at the Royal Academy, survives as a memento of this period. Subsequently he joined the late F. A. Manning, well remembered as a specialist in matters relating to anthracene, in whose laboratory he spent a large part of his life. In 1893 he re-established himself in independent analytical and consulting practice in St. Andrew's Hill (his "Den No. 3"), where he continued to work at anthracene, but also largely concerned himself with investigations relating to non-ferrous alloys, as well as with miscellaneous consultative work, in which he was engaged almost up to the time of his death.

Bassett contributed in his earlier years several papers of interest to the Transactions of the Society. The first of these was on "Tetrabasic Carbonate of Ethyl" (1864). In 1865 he contributed

a "Note on the Action of Chloropicrin and Chloroform on Potassium Acetate"; *in 1866, a paper on "A Cyanogen Derivative of* Marsh Gas"; in 1867, a paper on "Julin's Chloride of Carbon"; and, in 1872, a paper on "Eulyte and Dyslyte." As far as the Transactions are concerned he was then silent until 1890, when he contributed a paper on the "Interaction of Iodine, Water, and Potassium Chlorate." The Abstracts of our *Journal* give summaries of various other papers chronicling experimental investigations published in the *Chemical News*, including "Reactions of Tin with Sulphuric Acid" (1886), "Preparation of Trichloromethyl-Sulphuric Chloride" (1886), "Analysis of Anthracene" (1895), and "Reduction of Chromic Acid by Acetic Acid and its effect on Anthracene Testing" (1899); and also of a paper (1892) on the "Tabular Expression of the Periodic Law."

Bassett was fond of artistic society and a lover of music, being for many years an active member of the Royal Amateur Orchestral Society, in which he played the trumpet—an instrument in the construction of which he interested himself to the extent of devising improvements therein.

He was married in 1879 to Mary Kate Colchester, who happily survives him, and left two daughters and one son, Dr. Henry Bassett, who is Professor of Chemistry at University College, Reading.

B. D.

JOHN CANNELL CAIN.

BORN SEPTEMBER 28TH, 1871; DIED JANUARY 31ST, 1921.

By the death of Dr. John Cannell Cain, which occurred suddenly at his residence in Brondesbury Park on the morning of January 31st, the Society lost an editor who for the past fifteen years had carried out the duties of his office with conspicuous ability and success. He was born at Edenfield near Manchester on September 28th, 1871, and was the eldest son of the Rev. Thomas Cain of Stubbins, Lancashire. At an early age he entered the Manchester Grammar School, that nursery of chemists which was destined under Mr. Francis Jones to supply so many men, ultimately to reach high positions, to the chemical schools of his time, and in due course entered the Owens College, where he studied chemistry under H. B. Dixon, who three years before had succeeded Roscoe in the chair of Chemistry. He obtained the degree of B.Sc. in 1892, and in the autumn of that year proceeded to the University of Tübingen where, after twelve months' work, he graduated with the degree of D.Sc. After that he worked for one semester at Heidelberg under Victor Meyer, and it was here that the writer first made his

acquaintance. In 1894 Cain returned to the Owens College, where two years previously W. H. Perkin had succeeded Schorlemmer in the chair of Organic Chemistry, but he does not appear immediately to have taken up organic research, because when the writer went to Manchester in the autumn of 1895 he found that Cain had been working for the past year with W. A. Bone, who was then starting his researches on gaseous combustion, work which was subsequently to appear in 1897 under their joint names in the paper entitled "The Explosion of Acetylene with Less than its Own Volume of Oxygen."

In 1895 Cain definitely chose the branch of chemistry to which he ultimately devoted his life by accepting the post of research chemist to Messrs. Levinsteins, Ltd., where he remained until 1901. It was during this period that the writer became intimately acquainted with him, because until Cain's marriage in 1898 they occupied lodgings in the same house at Cheetham Hill; and although their work led them in opposite directions, the writer going to Perkin's laboratory at the Owens College and Cain going to Crumpsal, nevertheless the evenings afforded opportunities for numerous discussions on the subject of colour chemistry, discussions which led to an agreement to write the text-book which subsequently appeared in 1905 under the title of "The Synthetic Dyestuffs," now passing through its fifth edition. The memories of those days are very pleasant, because Cain had a very lovable disposition and was a firm and true friend. One remembers among other things his genuine distress at the protests of the landlady who, doubtless incited by the neighbours, complained bitterly of the abominable smells which pervaded the house and neighbourhood. She certainly had just cause for complaint, for the Perkin school was at the time engaged on work with the unsaturated fatty acids, and Levinsteins were at the moment interested in α-naphthylamine. It is scarcely possible that anywhere else in the world the same house could have sheltered two people working with materials possessing greater affinity for human garments and more capable of rendering them intolerable to anyone in their immediate neighbourhood. Incidentally, one remembers the late Mr. Ivan Levinstein explaining to the Local Authority that α-naphthylamine was an aromatic substance and therefore quite incapable of producing the nuisance described.

In 1901 Cain decided to abandon for a time his work on the industrial side of his subject and to accept a teaching post which would enable him to devote time to research of a more fundamental character. With this object in view he became head of the Chemistry and Physics Department of the Municipal Technical School at Bury in Lancashire, a post which he occupied until 1904. During this

period, in association with Frank Nicoll, he published the first three parts of the series entitled "The Rate of Decomposition of Diazo-compounds," in which he showed the vast difference in the rate of decomposition of comparatively similar diazonium salts. Part I, published in 1902, dealt with the benzene series, and Parts II and III, published in the following year, with the naphthalene series, and with the temperature coefficient, respectively. During this period he also started a series of researches on "The Diazo-reaction in the Diphenyl Series," and published Part I, "On Dianisidine and 3 : 3′-Dichlorobenzidine," in 1903, Part II, "On Ethoxybenzidine," appearing in 1905. In 1904 Cain was awarded the degree of D.Sc. in the Victoria University of Manchester, and in the same year left the Bury Technical School, again entering the industry as Manager and Head Chemist to Messrs. Brooke, Simpson and Spiller of London, a post he occupied until 1906, when he was appointed Editor of the Society's publications.

During the fifteen years he held the editorship he found time to continue many of the researches he had commenced at Bury and to start new ones. For example, after publishing a number of smaller papers dealing mainly with the chemistry of the colouring matters, he began a new series called "Stndies in the Diphenyl Series," Part I of which was published with Percy May in 1910. Part II, which was published in 1912 with Albert Coulthard and Miss Micklethwait, described a hitherto unobserved form of isomerism possessed by benzidine derivatives, showing, for example, that there were two distinct dinitrobenzidines yielding distinct acetyl derivatives and distinct dinitrodiphenyls. It was suggested that this form of isomerism depended on the limitation of free rotation of the singly linked carbon atoms, and its occurrence has been further demonstrated by the recent work on the corresponding dicarboxylic acids by Kenner. The writer remembers discussing this problem with Cain at the time, and it was agreed that if the two carbon atoms joined by the single valency are asymmetric, as in all probability they are, the isomerism would be of the same type as that of the tartaric acids or of the *s*-dialkylsuccinic acids and would represent true *cis*- and *trans*-forms. It would therefore be interesting to ascertain whether either one of the two isomeric dicarboxylic acids is capable of being resolved into optically active enantiomorphs. The stndies of diphenyl compounds concluded with Part III, published with Dr. Brady in 1912, on diphenyl-diphthalamic acid.

In 1907 Cain advanced his theory of the constitution of the diazo-compounds and followed this in 1908 by a text-book, now in its second edition, on "The Chemistry of the Diazo-compounds,"

in which he deals with the whole of this subject in a concise and interesting manner. His theory, which involved para linkage, has not found universal acceptance, but neither for that matter has any formula of the diazo-compounds, excepting, perhaps, that of Blomstrand, which is undoubtedly the worst that has been suggested, if it be held that the formula of an organic substance should represent the simplest expression of its reactions. On this basis Cain's formula is greatly preferable to that of Blomstrand, which, as far as the writer is aware, has not one single shred of direct chemical evidence to support it. His literary work also included a volume on "The Manufacture of Intermediate Products for Dyes," published in 1908 and now in its second edition. He also left the almost completed MS. of a sister volume on the manufacture of dyes, which the writer hopes to complete for the press at an early date. Moreover, he wrote several of the articles on colouring matters and related subjects in the last edition of Thorpe's "Dictionary of Applied Chemistry," and also in the edition which is now passing through the press. More recently he undertook to revise "Roscoe and Schorlemmer" and volume I appeared shortly before his death.

Cain brought to the work of his editorship a remarkable knowledge of chemical data which his retentive memory had stored up throughout an active life. Probably no one else had a greater knowledge of the facts of organic chemistry, and on questions of nomenclature his word was final. Contributors to the *Journal* could not fail to be struck by his wonderful grasp of even the minor details of a paper, and it would often happen that an author's attention would be directed for the first time by the editorial red ink to the fact that previous work, which he had overlooked, had been published on the subject of his paper. The publications of the Society for the past fifteen years remain as a record of his devotion to the duties of his office.

During the war Cain placed his services where they were most required, and early in 1915 he was asked by the late Lord Moulton to act as his first inspector of explosives. He subsequently became manager of H.M. Factory at Hackney Wick, and later entered British Dyestuffs, Ltd., as chief chemist to the Dalton Works at Huddersfield. As a member of the technical committee of British Dyes he took an active part in the reorganisation of the dyestuffs industry in this country. His intimate knowledge of the theory and practice of dyestuff chemistry not only rendered his services of the highest importance in this connexion, but also caused his advice to be sought by the Department of Explosives Supply on many questions relating to the manufacture of explosives. His many-sided activities during this period, involving as they did the expend-

iture of great energy and skill, combined with the worry attached to considerable responsibility and the fatigue caused by long train journeys, undoubtedly contributed directly to bring about his early death, because he had a serious breakdown in 1915 which left permanent heart weakness. Nevertheless he was ever ready to help, and did not hesitate to undertake, at the request of the Chemical Warfare Department, the task of compiling a complete card index of all chemical substances possessing toxic or noxious properties. He was engaged in this work for the reconstituted Chemical Warfare Committee at the time of his death, and the writer has reason to know that his work in this connexion was carried out with the thoroughness which characterised all his actions.

Cain was a good lawn-tennis player and a keen cyclist, but his activities in these directions were sadly curtailed after his first heart attack; nevertheless he found solace in fishing, at which he was no mean craftsman, and in motoring. In 1898 he married Miss Amy Brown, who survives him, and he leaves two children, a son and a daughter, the former being just about to complete his training as an engineer at Cambridge.

During the past eighteen months the writer has had many opportunities of meeting Cain, because, with his usual willingness to help, he had agreed to collaborate in designing a new laboratory for semi-large scale production which has now been erected in the organic department of the Imperial College.

It is a matter of the deepest regret that he did not live to see the completion of a scheme which he had so much at heart and which he did so much to render practicable. J. F. T.

ARMAND GAUTIER.*

By the death of Emile Justin Armand Gautier, at Cannes, in his eighty-third year, France has lost one of her most distinguished chemists. Born at Montpellier, the son of a medical man, Gautier appears to have been destined to follow his father's profession, and to his early training is to be attributed, in all probability, the direction of much of his subsequent life's work in science, notably in biological chemistry. As a youth he obtained a post, under the Faculty of Montpellier, first as *aide-préparateur* and then as *préparateur* in the chemical laboratory; here he remained five years, and thus acquired that power and facility of manipulation which characterised his experimental work. In the early 'sixties he decided to attach himself to chemistry as a career. At that period the science was experiencing profound changes,

* Reprinted, by permission, from *Nature* (September 16th, 1920).

and chemical theory was developing with remarkable rapidity, more particularly owing to the progress in organic chemistry. Wurtz was everywhere recognised as one of the pioneers and leaders of the new movement, and accordingly young Gautier repaired to Paris to work under his inspiration and direction. At Paris he remained, becoming, in 1869, a member of the Faculty of Medicine, in 1872 director of the first laboratory of biological chemistry instituted in France, and in 1884, on the death of Wurtz, professor of medical chemistry. He was elected a member of the Academy in 1889.

During the fifty years of his scientific activity Armand Gautier published an extraordinary number of memoirs—upwards of 600, it is said. They range over every department of the science and practically every sub-section of it. Many of them, of course, are not of first-rate importance, but, collectively, they serve to show his breadth of sympathy, his receptivity, his intellectual keenness, his versatility, and the many-sidedness of his interests.

Here we can deal only with Gautier's more noteworthy contributions to the literature of chemistry. The influence of Wurtz is stamped on the earliest of them—as in his work on cyanogen derivatives, on the nitriles and their isomerides, the carbylamines—which mostly appeared in the Bulletin of the French Chemical Society, and served to establish Gautier's position as one of the foremost investigators of the new French school. His appointment as director of the laboratory of biological chemistry, already referred to, gave a fresh impetus and a new departure to his work as an investigator. In 1872 he signalised the existence of a class of cadaveric alkaloids, termed by Selmi *ptomaines*, and presumed to be products of putrefaction. Earlier investigators, such as Panum, Dupré, and Bence Jones, Marquardt, Schmidt, Bergmann, and Schmiedeberg, Zuelzer, and Sonnenschein, had obtained so-called putrefaction bases which occasioned physiological effects similar to certain vegeto-alkaloids. Selmi's term was adopted by Gautier to denote alkaloidal substances formed in the putrefaction of proteins. The earlier literature relating to the ptomaines —a term now fallen into disuse in scientific nomenclature—is full of errors, and there is practically no evidence that what is called "ptomaine poisoning" is due to poisonous alkaloids: it is rather to be attributed to bacterial infection and is caused by bacterial toxins. Gautier found in fresh tissues a number of basic substances, related to uric acid and creatinine, which he regarded as the products of ordinary metabolism, and to which he gave the name of *leucomaines*, to distinguish them from the products of bacterial action.

A subject which engaged Gautier's attention for some time, and to which he occasionally returned, was the widespread diffusion of arsenic in the animal organism, which led to work on improved methods of detecting and estimating that element in microchemical quantities. His speculations concerning the rôle played by arsenic, as well as by iodine, in our organism may be said to be at the basis of modern therapeutics. The question of the influence of the infinitely little on hygiene had, in fact, a special attraction for him. It is seen in his work on the action of the impurities of the air of towns on the public health. He detected the constant presence in air of iodine, as well as of hydrogen; the former, he imagined, was due to the presence of microscopic algæ, the latter to emanations from primitive rocks, volcanoes, and thermal springs.

Gautier, as a biochemist, also engaged himself in questions of plant physiology, and on the chemical transformations of various products in the life-history of vegetable organisms. These studies occasionally took a practical turn, as, for example, in his inquiries into the colouring matter of the grape and the detection of the fraudulent colouring and dilution of wine, and the influence of "plastering," "collage," and fortifying on the weight of the dry extract. The nature of tobacco-smoke also attracted his attention. He found that when tobacco is smoked in a pipe the volatile liquid products consist mainly of basic compounds, among them nicotine, a higher homologue, $C_{11}H_{16}N_2$, which pre-exists in tobacco leaf, and a base, C_6H_9ON, which appears to be related to picoline. Hydropyridines and other alkaloids are also present, resulting from the decomposition at relatively low temperatures of the carbopyridic and carbohydropyridic acids present in the leaf.

Gautier was a fellow-worker with Maxwell Simpson in Wurtz's laboratory, and the two collaborated in the study of the action of hydrocyanic acid upon aldehyde. He was an occasional visitor to this country, and represented France at certain academic gatherings in London. He was a genial soul, and, as was said of him by M. Deslandres, president of the Academy of Sciences, when pronouncing his *éloge*, remained young in spirit and young of heart until the end.

T. E. T.

WILLIAM HERBERT PIKE.

BORN JULY 3RD, 1851; DIED FEBRUARY 8TH, 1921.

WILLIAM HERBERT PIKE, a life member of the Chemical Society, son of Warburton Pike, barrister-at-law, was born at Brixton in 1851 and was educated at Rugby. Thence he went in 1869 to King's College, London, to study chemistry under the late

Professor Bloxam, and afterwards to the Normal School of Science, South Kensington, where he worked under Guthrie. He then proceeded to the Polytechnic Institute in Vienna and afterwards to Berlin, where he studied for two years under Hofmann, taking his doctorate at Göttingen. On returning to England he worked for a short time in London and was elected a Fellow of the Society in 1874. He was appointed to an Assistantship at Oxford by the late Professor Odling and became a Lecturer on Chemistry at Merton College and was made M.A. of the University. On the creation of the University College of Toronto in 1880, Oxford was requested to staff the professoriate, and Dr. Pike was selected for the professorship of chemistry. In the early days of the College the provision for teaching practical chemistry compared very unfavourably with the places in which Pike had been trained. He soon, however, induced the authorities to furnish him with a properly designed building, which his talent for mechanical construction enabled him to equip in a suitable manner. During the first years of his professorship, the whole of his time and energies during the College Sessions were occupied with the routine duties of his chair and in the establishment and direction of the graduating school of chemistry and physics. An explosion in the laboratory when attempting to prepare the highly unstable manganese trioxide deprived him of his right eye and for a time wholly incapacitated him for research work.

On his retirement from the University College after nearly twenty years' service, Dr. Pike took up his residence at Salcombe, South Devon, and lived the life of a country gentleman. He took an active interest in local affairs, was elected a member of the Urban District Council, on which he served as chairman for a number of years, a position for which his knowledge of affairs, sound judgment, and business aptitude rendered him well qualified, and became a justice of the peace for the County of Devon, and a regular attendant on the Kingsbridge bench. He occupied his leisure in mechanical pursuits and fitted up a well-equipped engineering workshop. He was an ardent motorist and followed the development of motor engineering, with which he had considerable practical acquaintance, with the liveliest interest. During his college vacations he travelled over considerable sections of Canada. He was a cousin of the great Canadian explorer and big game hunter, and he himself acquired a reputation as a sportsman whilst in Canada. He maintained his interest in sport at Salcombe, and regularly shot over the country in the neighbourhood.

All Pike's contributions to the literature of chemistry appeared before his appointment to Oxford—that is, during 1873 and 1874.

He worked with Biedermann on cresotic acid (*Ber.*, 1873, **6**, 233) and published a short paper on benzoyl-sulpho-urea (*Ber.*, 1873, **6**, 755) and an uncompleted investigation on the homologues of oxaluric acid (*Chem. News*, 1873, **28**, 173).

During the last few months of his life Pike's health gradually failed. He died in his sleep on February 8th, 1921, and was buried at Salcombe.

T. E. T.

JOHN RUFFLE, F.I.C.

BORN 1843; DIED NOVEMBER 19TH, 1920.

JOHN RUFFLE, who died at Ware on November 19th, 1920, in his seventy-eighth year, had been a member of the Society since 1872. He was a native of Suffolk aud spent part of his early life in Germany, where he became interested in farming. On his return to England he became a student at the Royal Agricultural College at Cirencester. After taking his diploma he remained as chemical assistant to the then Professor of Agricultural Chemistry in the College, the late Dr. Augustus Voelcker, consulting chemist to the Royal Agricultural Society, and after spending some years in his laboratory he became chemist in the Fertiliser Works of Messrs. James Gibbs & Co. at Silvertown, where he stayed until 1884. After practising for a few years as a consultant in London he went to South Wales as chemist to the "Cape Copper Company and Butenferry Chemical Works" at Neath, where he stayed until 1896. He then joined the chemical staff of Messrs. Allen and Hanbury, Limited, at Ware, where he worked until the close of his life. Ruffle made an important contribution to analytical chemistry in a well-remembered paper on the "Estimation of Nitrogen by Combustion, including Nitro-Compounds," published in the *Transactions* of the Society in 1881, in which he showed that the admixture of sulphur with the material to be analysed and of sodium thiosulphate with the soda-lime, in the Will and Varrentrap combustion process, resulted in complete reduction of nitric nitrogen to ammonia, euabling the analyst to determine in one operation the nitrogen present as nitrates, together with organic and ammoniacal nitrogen, in a complex fertiliser. The process has not been surpassed for accuracy by the more modern "moist combustion" process of Kjeldahl and Jodelbauer (modified by Gunning and Arnold), which has now conveniently replaced it in most agricultural laboratories, and there are many chemists still at work who have grateful recollection of the help afforded them by Ruffle's work. During the time at which he was especially engaged with chemical fertilisers he made some valuable investigations on

the constitution of superphosphates, showing that the prevalen theoretical views on their composition were incorrect. His paper on this subject were published in the *Journal of the Society c Chemical Industry* in 1887, and he contributed to the same journa and to other periodical literature, many occasional notes of interes on current chemical topics.

Owing to continued absence from London for the last thirt years Ruffle was almost forgotten as a once active member of th Society, but he kept in touch, by correspondence, with some c his earlier chemical colleagues, and many of these are still livin to mourn the loss of an affectionate and most lovable friend. H was a widower and left one son, Mr. Hugh W. E. Ruffle.

B. D.

CHARLES SIMMONDS.

BORN DECEMBER 19TH, 1861; DIED JANUARY 15TH, 192]

CHARLES SIMMONDS was born at Stourbridge in 1861 and enter the Customs Branch of tho Civil Service in 1883, being transferr three years later to the Inland Revenue Department, which at th time had control of the Excise duties. In the following year l obtained one of the eight scholarships which the Commissione offered annually to approved Revenue Assistants. This ga Simmonds the opportunity he sought—training at the Royal Colle of Science and an assistantship in the Somerset House Laboratory

Simmonds's career at South Kensington was one of signal succe and after some years as assistant, during which he graduated in scien at London University, he received appointment to the permane staff of the Laboratory. At the time of his death he was one the Superintending Analysts.

Sir Edward Thorpe became principal of the Laboratory in 18(and three years later the staff entered into new premises at Clemen Inn Passage. In 1909, Sir James Dobbie succeeded Sir Edwa Thorpe, and in 1911 became the first Government Chemist of t new separate Government Department.

Both these principals recognised Simmonds to be a man of mark ability and capable of carrying out work of the utmost importan One of the earliest special investigations placed in his hands was inquiry into the composition of pottery glazes and fritts for t information of the Royal Commission appointed to report on th subject. Arising out of this work, several papers were contribut to the Society's Journal—"Lead Silicates in Relation to Potter (1901), "Constitution of certain Silicates" (1903), "Redu Silicates" (1904), as well as an article in Thorpe's "Dictionary

Applied Chemistry" on "Pottery Glazes," and (in conjunction with Sir E. Thorpe) a paper on the "Influence of Grinding upon the Solubility of Lead in Lead Fritts" (*Manchester Memoirs*, 1901).

The investigation on pottery glazes was followed by an inquiry into the changes which take place in milk on souring, for the purposes of the duties thrown upon the Laboratory by the Food and Drugs Act. This work had been previously carried out to some extent by Lewin, but several points required elucidation. The results of the inquiry were communicated by Sir Edward Thorpe to the Society in 1905.

For some years Simmonds was engaged in the analysis of samples referred by justices from courts of law in disputed cases under the Food and Drugs Act, but his work for the past ten or twelve years was more particularly concerned with drugs, pharmaceutical compounds, and spirituous preparations. In this connexion he carried out for a Parliamentary Committee the analysis of a large number of secret remedies. During this time he communicated several papers to the Society of Public Analysts, for example, "The Determination of Small Quantities of Methyl Alcohol" (1912), "The Estimation of Strychnine in the Presence of Quinine" (1914).

The war brought him a great amount of work relating particularly to alcohol, and its suggested use for power purposes. He perceived the lack of a comprehensive manual dealing with alcohol, and produced during this period of great pressure his treatise on "Alcohol," which was published in 1919. For his war services he was appointed an officer of the Order of the British Empire.

Simmonds was pre-eminently an analyst. Although he had considerable literary attainments—he was a frequent contributor to *Nature*—and showed by his papers in the Society's Journal that he was at home in the realm of theoretical chemistry, it was in analytical manipulation that he excelled. The extreme care which he took to ensure that his apparatus was clean, and calibrated, that the solutions he used were standardised, and that a note was made of everything that was to be observed in a test, were features which distinguished all his work.

The Laboratory where he laboured so long has been enriched by new processes, by many modified and improved methods, and by the upholding of the importance to be attached to every minute detail of analytical procedure.

Simmonds's end was sudden and entirely unexpected by his colleagues and friends. At work as usual one day, he had a heart attack during the night, and passed away twenty-four hours later.

Simmonds leaves a widow and two young children. A son by a former wife has attained a position in Australia as a journalist and author.

G. STUBBS.

BERTRAM JAMES SMART.

BORN 1882; DIED SEPTEMBER 4TH, 1920.

THE death of Bertram James Smart, B.Sc., at the early age of thirty-eight, has removed a promising investigator from the chemical world. His originality of thought and indefatigable energy enabled him to cover a wide field of research.

His early training was received at the Mathematical School, Rochester, and he commenced his chemical career at Guy's Hospital as an assistant to Sir Thomas Stevenson and Dr. Wade. In February, 1903, he was engaged as a member of the newly-formed research staff at the Royal Arsenal, Woolwich, under the Explosives Committee, and distinguished himself by his capabilities. His work was concerned mainly with explosives, but he also carried out valuable investigations on alloys. He published papers jointly with Silberrad on the removal of nitrous acid from nitric and sulphuric acids (*J. Soc. Chem. Ind.*, 1906, **25**, 156), the action of methyl and benzyl iodides on nitrogen iodide (T., 1906, **89**, 172), and the preparation of bistriazobenzene (T., 1906, **89**, 170).

In 1907 Smart was deputed to go to Hongkong to undertake an investigation into the stability of propellants stored in hot climates, and after six months he proceeded with similar tests at Sydney, N.S.W. On returning to Woolwich in 1908 he continued his work on the stability of nitric esters with special reference to the true significance of the Abel Heat Test. A paper on this subject by Robertson and Smart appeared in 1910 (*J. Soc. Chem. Ind.*, 1910, **29**, 130). In this year also he graduated as B.Sc. at the University of London.

Smart's metallurgical work at Woolwich did not form the subject of any published papers, but it led in 1911 to his appointment by the Government of New South Wales to organise the manufacture of iron and steel in that State, and subsequently he was placed in charge of the Testing Branch of the Department of Public Works at Lithgow, N.S.W. He continued to take an active part in scientific work, and was for some years chairman of the Sydney Section of the Society of Chemical Industry. Papers were published by him from Sydney on the Abel Stability Test, the volatility of arsenious oxide from hydrochloric acid solutions, and the suitability of Posidonia fibre for conversion to gun-cotton (*J. Soc. Chem. Ind.*, 1913, **32**, 967; 1914, **33**, 900; 1918, **37**, 300T).

His death occurred on September 4th, 1920, at Sydney, and its notification will have been received with regret by many fellows, by whom he was held in high esteem, not only on account of his scientific ability, but also for his personal characteristics.

R. C. F.

BERTRAM BLOUNT.

BORN 1867; DIED APRIL 9TH, 1921.

BORN within sound of Bow Bells, Bertram Blount had a hard struggle to retain his hold upon life in early childhood. By the time he was sixteen, however, he had made good his lost schooling and left King's College School with honours in the Matriculation Examination of the University of London. He entered the Chemical Laboratory at the College, then under the direction of the late Professor C. L. Bloxam, from whom he imbibed that love of analysis which, he subsequently maintained, is the primary qualification for a chemist. At nineteen years of age he was ready to support himself, and accepted service as assistant to Mr. W. H. Stanger, a consulting engineer to the Crown Agents for the Colonies. It soon became known to Stanger's clients that the chemical testing of constructional materials is as valuable as the mechanical testing, and in a very few years the practice developed to include that of consulting chemist with Blount as partner. The combination was a happy one, but comparatively brief, owing to the death of Stanger. Blount continued in practice on his own account and was very soon in the front rank as a consultant, the chemistry of cement being his chief subject.

Blount's skill in solving chemical problems was remarkable. His power of getting at the root of the matter appeared almost intuitive, although in reality due to his undaunted perseverance in meeting every difficulty. It was ever his wont to seek simple causes—to hold his imagination in check. In a sense this was necessary, because his mission in life was to find remedies for the troubles of the engineer. Had it been otherwise, had it been possible for him to give full play to imagination, we should have had in Blount a fine researcher. As it is, his contributions to scientific literature are not numerous, and are chiefly concerned with the chemistry of cement and with points of analytical practice. His first publication was in this *Journal* (1885); some friend had sent him a sample of explosive pyrites, and the paper deals with the cause of the explosiveness, attributing it, on satisfactory experimental data, to liquid carbon dioxide contained in cavities in the mineral. Blount's name does not again appear in the *Transactions* until 1917, when, having determined to relax his personal attention to his clients' interests and having devoted a room at home to a well-fitted laboratory, he entered on a course of experiments testing the capabilities of the balance. Later, in conjunction with J. H. Sequeira, he investigated the origin of the colour of Blue John.

The *Analyst* and the *Journal of the Society of Chemical Industry* contain the rest of his original work.

Blount was a clever writer, with a clear and incisive style; and his tongue was even as his pen. His more permanent writings are two text-books, "Chemistry for Engineers and Manufacturers" (with A. G. Bloxam) and "Practical Electro-Chemistry," a Monograph on Cement (with W. H. Woodcock and H. S. Gillett), and the articles on Cement in the "Encyclopædia Britannica," and Thorpe's "Dictionary of Applied Chemistry." His characteristic was his personality; careful about his assertions, he was careful to be assertive and generally carried conviction. It may fairly be claimed for him that his pertinacity was of great service to the country in 1915, when he insisted that the Government must make cotton contraband; few knew what the struggle really cost him in nervous energy, and it is likely enough that his steady failure in health during the years that have intervened was in part due to his effort then. He died on April 9th, regretted by the many who found him a boon companion and a staunch friend; he never became domesticated.

Blount joined this Society in 1890; he was a Fellow of the Institute of Chemistry and of the Society of Public Analysts, on the Councils of which bodies he did good service, acting as Examiner for the Institute for several years. He was one of the founders of the Faraday Society, and a well-known Associate of the Institution of Civil Engineers. A. G. B.

ALEXANDER WYNTER BLYTH.

BORN AUGUST 29TH, 1844; DIED MARCH 30TH, 1921.

ALEXANDER WYNTER BLYTH, who died in London on March 30th 1921, was the son of a surgeon of Woolwich and was educated a King's College, London, where he early showed his interest i chemistry. Having obtained the membership of the Royal Colleg of Surgeons, he devoted his attention to public health work an eventually became Medical Officer of Health and Public Analyst for St. Marylebone and Public Analyst for the County of Devon After occupying the dual appointment at St. Marylebone fo upwards of thirty years, he resigned the medical portion, remain ing Public Analyst until his death at the age of seventy-six.

Wynter Blyth was a man of great ability and untiring energ and in addition to occupying most of the honorary positions co nected with public health affairs, including the presidency of th

Incorporated Society of Medical Officers of Health and the Registrar of the Royal Sanitary Institute, he found time to become a barrister-at-law of Lincoln's Inn and to write four or five books on hygiene and public health.

As a chemist, Wynter Blyth was best known as the author of two standard works—"Foods: their Composition and Analysis," and "Poisons: their Effects and Detection." Both have passed through several editions, the last, on poisons, in the preparation of which he was assisted by his son, having only recently been published, and his death found him in the midst of the revision of "Foods," another edition of which was shortly to be issued. For both these books he did a large amount of original chemical work in the investigation of new processes or in the attempt to improve the older ones described therein, his most recent researches dealing with the reactions of the alkaloids and the separation of the acids of butter-fat. He was also engaged in experiments on micro-crystallography and was keenly interested in spectroscopic work. He was one of the pioneers of bacteriology in this country.

Outside his work Wynter Blyth took a lively interest in everyday affairs, was a genial companion, an enthusiastic motorist, and latterly a not unsuccessful farmer.

As a man of his energetic temperament would wish, Wynter Blyth died quite suddenly in the midst of his work. He leaves a son and two daughters and a large number of friends to mourn his loss, amongst the latter being many who were much indebted to him for the help and kindness he was ever ready to extend.

J. K. C.

SIR LAZARUS FLETCHER.

BORN MARCH 3RD, 1854; DIED JANUARY 6TH, 1921.

SIR LAZARUS FLETCHER was born at Salford on March 3rd, 1854, and was the eldest of a large family of brothers, five of whom survive him. His father, Stewart Fletcher, was in humble circumstances, but was a man of much grit. In spite of the *res angusta domi* Lazarus Fletcher succeeded in getting his education at the Manchester Grammar School under the late F. W. Walker; and with the aid of a Brackenbury Scholarship he graduated from Balliol College, Oxford, with first classes in the schools of Mathematics and Natural Science. He was highly distinguished in the Junior Mathematical Scholarship in 1874, and two years later he gained the Senior Mathematical Scholarship in the University. He then became Demonstrator in Physics under the late

Professor Clifton, 1875—1877, and Millard Lecturer in Physics (Trinity College) 1877—1878. In 1877 he was elected to a fellowship at University College, which he vacated in 1880 on his marriage with Agnes, the daughter of Rev. Thomas Holme, of Moorside, Oldham.

In 1878 he became First Assistant under the late Professor Nevil Story-Maskelyne in the Mineral Department of the British Museum, and in 1880 he succeeded Maskelyne as Keeper. On the retirement of the late Sir William Flower in 1898 from the Directorship of the Natural History Departments of the British Museum, Fletcher was marked out to succeed him, but owing to the action of certain prominent zoologists he was passed over, and Sir E. Ray Lankester was appointed. In 1907 the latter retired when Fletcher was in very indifferent health, and no appointment was made for nearly two years. At last, in 1909, Fletcher became Director. He held the directorship until 1919, when the state of his health, which had been very precarious since a breakdown in 1906, compelled him to send in his resignation. On this occasion the Trustees passed a special vote of thanks, in which they recognise his eminent services to science, his loyalty to themselves, and his unselfish devotion to the promotion of harmonious relations amongst the Staff.

At the time of Fletcher's first appointment the collection of minerals was on the point of being transferred from Bloomsbury to the new building in Cromwell Road, and naturally his time was mainly occupied with the duties connected with the safe transference of the specimens.

His first paper is that read at the Crystallological Society and published in the *Philosophical Magazine*, 1880, [v], **9**, 80, on "The Dilatation of Crystals on Change of Temperature." On the assumption that the physical and geometrical properties along all parallel lines in a crystal are the same, he shows that the planes of symmetry must remain unaltered, and that the rational (or even irrational) value of the anharmonic ratio of four tautozonal planes (first established by W. H. Miller) is unchanged; further that, as a sphere at one temperature becomes an ellipsoid at another, there is one triad of lines which are at right angles at both temperatures (Neumann's *thermic* axes). He also proves that one triad of lines (not necessarily at right angles to one another) remains fixed in space (*atropic* lines), and that an infinite number of triads maintain their mutual inclinations unchanged (*isotropic* lines). In anorthic crystals these several triads have no apparent connexion with one another or with the crystallographic axes; and in the oblique system one thermic axis and one atropic line are alone fixed, being coincident with the dyad axis of the crystal. But although each set of triads

established for the two definite temperatures, they are not necessarily the same for other temperatures; although as the changes of temperature are gradual one naturally expects each set to undergo a gradual variation from one position to another.

At the instigation of Professor von Groth the theory was tested by J. Beckenkamp but with unsatisfactory results, the most surprising one being that in a crystal of anorthite the minimum thermic axis for the pair of temperatures 20° and 80° varied by 26° 32′ from its position for the pair 20° and 200°. This unexpected variation gave rise to Fletcher's second paper on the subject, which was published in three parts (*Phil. Mag.*, 1883, [v], **16**). He begins by a criticism of the Neumann formulæ employed by Beckenkamp. They seemed to him unnecessarily complex and likely to lead to errors, so he proceeds with consummate skill to work out the equations needed for the determination of the relations of the several sets of triads; and lastly he tests their accuracy with the aid of Beckenkamp's measurements of gypsum and anorthite. The computations are very laborious, but his formulæ bring out results closely accordant with those of Beckenkamp, and he establishes the change of position through 26½° of the minimum thermic axis of anorthite, mentioned above, and leaves it unexplained. But are crystals ever so ideally perfect as to give data sufficiently accurate for such investigations?

Another of his physico-mathematical memoirs is that on "The Optical Indicatrix and the Transmission of Light in Crystals (*Min. Mag.*, 1891, **9**, 278), which with some additions was afterwards published separately by Henry Froude of the Clarendon Press. The Indicatrix is an ellipsoid the principal axes of which are inversely proportional to the principal indices of refraction, and is identical in form with the ellipsoid of elasticity of several authors and with the ellipsoid of polarisation of Cauchy. By means of it Fletcher deduces all the principal phenomena of transmission which have been observed. The analysis is a model of skilful handling of problems of analytical geometry. In the introduction he points out that Fresnel's deduction of the wave-surface was the result of happy generalisation, and is really independent of the inconsistent set of assumptions on which he afterwards based it. As in other cases, Fletcher's introduction is a lucid statement of the steps by which our present knowledge of the subject has been acquired, and can be readily followed without much special study.

But the work by which he will be best remembered is the series of valuable memoirs on meteorites. They are of two classes: in one he investigates the history of several meteoric stones and irons—more especially those discovered in Atacama and Mexico. There

was much doubt whether several of them, variously labelled even in the same museum, belonged to one fall or to several different ones. Here his incomparable knowledge of geography was most helpful, and the minute care with which he followed every clue as to the history of a fragment, or of a complete mass, has done much to establish the true relations. This set of memoirs appeared in the *Min. Mag.*, **8**, 146 (Chartres), 223 (Atacama); **9**, 16 (Tucson), 91 (Mexico); **12**, 167 (Patagonia); and **14**, 28 (Great Namaqualand).

The second class of papers deals with the methods of chemical analyses and the determination of the constituents of meteorites. They are to be found in *Min. Mag.*, **7**, 121 (Youndegin), 179 (Nejed), 183 (Greenbrier); **10**, 287 (Makariwa); **13**, 1 (Zomba); and **15**, 147 on a possible compound, Fe_5Ni_3. The Makariwa and Zomba memoirs discuss the methods of analysis very fully, and are all but indispensable to anyone engaged in such investigations. They are clear in exposition and are critical in their estimation of the accuracy of the methods. But the mass of petty detail that has to be attended to is a great deterrent from such work. It is evident, however, that no detail was too insignificant for him if it conduced to accuracy in the result. His thoroughness is conspicuous in the investigation of the minute crusts of cubic forms named by him cliftonite—a form of graphite which seems to resemble the thin laminæ, recently described by Mr. J. R. Sutton (*Trans. Roy. Soc. S. Africa*, 1921, **9**, 87), which alternate with laminæ of clear diamond.

Fletcher's "Introduction to the Study of Meteorites," published by the Trustees of the British Museum as a guide to the Collection, is a useful text-book not only for beginners but also for the curators of museums, for under each meteorite is given either the date of the fall, when this is known, or a reference to the journal in which a full account of it is to be found.

He wrote two other guide-books—one to the Collection of minerals, the other to that of rocks. Both are really elementary treatises on the subjects, giving much information on the history of the Collections, as well as of the sciences they illustrate.

As Keeper his time was much occupied with administrative duties, and he had to make the selection of new acquisitions. He thus had opportunities of first perceiving new or rare minerals, but he generally passed them on for investigation by one or other of his able assistants, with all of whom he was on terms of close friendship. He took up, however, two difficult substances, of which one, daviesite, consisted of extremely minute crystals projecting from the sides of a cavity two millimetres across. Of these crystals he

determined the crystallographic and physical properties, and also proved them to be a lead oxychloride. The second, baddeleyite, was a single small crystal of native zirconia. His determinations had to be made without serious injury to the specimen, and were fairly complete. They have since been confirmed by the discovery and examination of an ample supply of fresh material.

His only contributions to the *Journal of the Chemical Society* consist of the determinations of the crystallography of two organic substances formed by W. H. Perkin (T., 1880, **37**, 548; 1881, **39**, 446); and of another organic compound obtained by Messrs. Bedson and King (T., 1880, **37**, 754).

In 1916 Fletcher was knighted, and in the same year he married his second wife, Edith, who had been the devoted nurse and helper of her sister, his first wife, during long years of delicate health until her death in 1915. Lady Fletcher and an only daughter survive him.

It is not necessary to dwell on the kindly nature of one who endeared himself to all his friends by his uprightness, sincerity, and unselfish loyalty, and delighted them by his quaint humour.

W. J. L.

DAVID HENRY NAGEL.

BORN NOVEMBER 10TH, 1862; DIED SEPTEMBER 27TH, 1920.

DAVID HENRY NAGEL was born at Dundee in 1862 and was educated at Dundee Institution and at Aberdeen University. In 1882 he was elected to a Millard Scholarship at Trinity College, Oxford, where he was to spend the rest of his life. As an undergraduate Nagel was distinguished by the breadth of his interests: not only did he find time to study other sciences besides his main subject, Chemistry, but in 1883 he gained the Taylorian Exhibition in German. He was also one of the founders of the Oxford University Junior Scientific Club, which has served a very useful purpose in bringing together men from different colleges engaged on different lines of scientific work. Nagel read Chemistry under Prof. H. B. Dixon (then Millard Lecturer at Trinity), and gained a first class in the Final Honours School in 1886. Two years later he was appointed Lecturer in Physics and Chemistry at Trinity, and in 1890 he was elected Fellow and Science Tutor of his College, of which he became Senior Tutor in 1907.

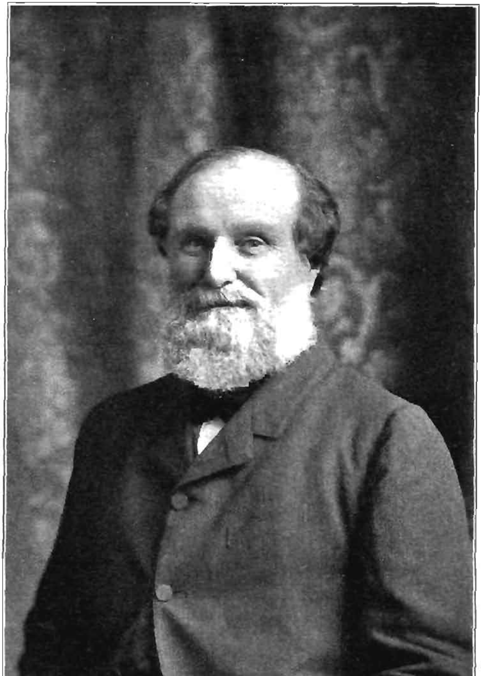
In the laboratory which Trinity shares with Balliol, Nagel acted as assistant first to Prof. H. B. Dixon, and afterwards to the late Sir John Conroy, but for the last twenty years he was mainly

responsible for its work. Intended originally as a College laboratory, its scope was extended in 1904, when the two Colleges undertook to provide a practical course in Physical Chemistry for all undergraduates reading for the Chemistry School, thus making it virtually a University institution. In the planning and supervising of this course Nagel's intimate knowledge of the physical aspect of chemistry and his skill in devising apparatus were invaluable. Successive generations of undergraduates owe much to his teaching. He was an admirable critic of laboratory work, with a quick eye to detect slovenliness or mistakes, but he was a most patient and kindly teacher, and would take endless pains to ensure that his students understood what they were doing, and why it should be done in a particular way.

Nagel had an encyclopædic knowledge of chemical and physical literature and of experimental methods, which was always at the disposal of his colleagues, who rarely went to him in vain for information and help, and his suggestions were almost invariably of practical value. Nevertheless he did hardly any original work, partly because he was too busy in other ways. But, as his former tutor has said of him, this was not the whole cause. "On one side there were difficulties, some lack of the fighting spirit, and, perhaps, a fear lest the road he chose to pursue might lead nowhere; on the other, there were his keen delight and critical appreciation of many lines of work, and the consciousness that his life would be more complete in unselfish devotion to others than in seeking fame for himself."

The outstanding feature of Nagel's mind was his breadth of view on any question in which natural science was concerned. He had an almost universal acquaintance with the sciences and an unusually clear vision of their relation to one another. It was this which gave him a unique position in the Science Faculty at Oxford. He was seen at his best as Chairman of the Board of the Faculty of Natural Science. The clearness with which he could define the point at issue, his well-balanced judgment, his patience and his tact will always be remembered with gratitude by his colleagues. He was a member of almost every Board and Committee in the Science Faculty, and he devoted himself unsparingly to the work of all these bodies; by his efforts to secure their due co-ordination he rendered a great service both to the University and to the cause of Science.

Many other forms of University work claimed a share of his attention. He took a keen interest in the development of women's education at Oxford. He was a delegate of the University Press, where his advice on technical points was of the utmost value. As



WILLIAM ODLING.

[To face Trans., p. 553.

a delegate for local examinations, and for the inspection and examination of schools, he exerted a considerable influence on the teaching of science in schools, and the fruits of his wide experience in this sphere were of great service to the Prime Minister's Committee on the Teaching of Natural Science.

In College his influence was felt everywhere, though exercised in a singularly unobtrusive way. His sympathetic and unselfish nature enabled him to understand and to get on with men of very varied types. In spite of the claims made upon him by his pupils and by his university work, his knowledge of all members of the College was astonishingly intimate, and a vivid interest in individuals enabled him to keep in touch with each successive generation. As a colleague he was delightful. It was impossible for him to cause offence or to make an enemy. His modesty almost amounted to a fault. No one could know him without placing reliance on his judgment. Always ready to discuss difficulties, great or small, he was at his best in helping others over stiles.

H. H.
H. A. P.

WILLIAM ODLING.

BORN SEPTEMBER 5TH, 1829; DIED FEBRUARY 17TH, 1921.

THE year 1829 goes back to early days in the history of chemical theory. Dalton's atomic theory was only twenty years old and Dalton himself was still living. Organic Chemistry, the youngest branch of the science, was not much older. Up to 1784 the composition of not a single organic compound was known; in that year Lavoisier proved that alcohol was a compound of carbon, hydrogen, and oxygen, and the chemistry of the carbon compounds had begun.

In 1829, Faraday gave his first Bakerian lecture, and Graham published his first researches on diffusion. Laurent had just started on his European tour after taking his diploma of engineering. Gerhardt, Williamson, Frankland, Wurtz, and Kolbe were still schoolboys. Kekulé was born in the same year.

George Odling, the father of William, was a medical practitioner in London, and became surgeon to the new police force. His son William was destined for the same profession, and after a private-school education entered Guy's Hospital in 1846. Two years later he passed his first M.B. examination at London University, obtaining gold medals for chemistry and materia medica. The chair in chemistry at Guy's Hospital was held by Dr. Alfred

S. Taylor, well known as a toxicologist. Odling passed his second M.B. examination in the first division in 1851 with honours in physiology and comparative anatomy. He never practised medicine for himself, but for a time helped his father with his practice. Although he never talked much about himself, he told his son how he came to give up a medical career for chemistry. It happened that a lecturer at the Royal Institution was taken ill and there was no one to take his place. Someone suggested that there was a young doctor at Guy's who was interested in chemistry and that they might try him. In the short time Odling had, he thought of nothing but the lecture day and night, and to such good purpose that, as he said when more than seventy: "I gave one of the best lectures I have ever given in my life, with the result that I was asked to give a course of lectures at the same place and was appointed lecturer in chemistry at Guy's Hospital." This must have been the lecture given at the Royal Institution in 1855 on "The Constitution of Hydrocarbons." He was a success at once, and had no long years of drudgery before recognition. His first book, a practical chemistry for medical students, was published in 1854 and went through five editions, the last in 1876. In the following year, 1855, the Cavendish Society published Laurent's "Chemical Method," translated into English by Odling. He then went to Paris and studied under Gerhardt, who, doubtless impressed, as all must have been, by Odling's kindly nature and charm of manner, wrote of him as "l'ami Odling." Odling became Secretary of the Chemical Society in his twenty-seventh year, and Fellow of the Royal Society in 1859, being elected at his first candidature. At his death he was the senior Fellow but one. He was also elected in 1859 a Fellow of the Royal College of Physicians. He was the first medical officer of health for Lambeth, until the year 1862. At Lambeth he had the experience of an epidemic of cholera. In one street he found that all the houses supplied by one company's water were free from cholera, while those supplied with water by the other company had cases of the disease. The former company supplied river water and the latter company water from a well which had been carelessly polluted. He was thus led to the belief that river water was the safer, because the natural purification was so great, whereas a well was easily contaminated and had not the same chance of purifying itself. Some years later he was appointed with Frankland to report on the Thames water between Kingston and Lechlade. They went up the river in a launch, taking samples of the water on the way. They found that the water became less pure the higher up the river the samples were taken. Frankland at first held that the Thames water was too impure to be fit for drinking, but Odling considered

that the natural purification that went on in a river was so great that it was safe to drink Thames water anywhere, and with this opinion Frankland ultimately agreed. Frankland and Odling went other and more adventurous cruises in the yacht "Sophia," which Frankland kept at Cowes. One adventure is related in Frankland's life:

"Landed with Odling at Yarmouth, walked to Alum Bay, scrambled over the base of the cliffs at dead low water to the Needles and into Scratchell's Bay. Tide began to come in rapidly, the water, having covered ledges of rock upon which we had stepped, rendered our return difficult; however, this was overcome by dint of wading until we came to a projecting ledge of rock, against the face of which the waves were dashing furiously with a mean depth of water of about 5 feet. This looked formidable, but nature did not desert her disciples in the hour of need, but opened a cleft in the rock through which (neither of us fortunately being aldermanic in our shape) we could just squeeze ourselves and thus elude the treachery of the waves."

Odling was for many years associated with Crookes and Tidy as examiner of the London Water Supply. He served as a juror at many of the exhibitions in London, in Paris, and in America. His advice was much sought after in legal cases. He condemned, in 1857, the mode of treating the London sewage employed at that time. It consisted in mixing lime with the sewage and discharging the mixture into the river. He was sceptical as to the supposed efficacy of the process, and claimed that, if it was employed at all, the sludge ought to be removed before any discharge into the river. He also condemned the proposed use of ferric chloride for the treatment in the same way of London sewage.

In 1863 Odling was appointed to the chair of chemistry at St. Bartholomew's Hospital, in succession to his friend Frankland. This was his first independent post. At Guy's he had been demonstrator under Taylor. Five years later he succeeded Faraday, who had died in 1867, as Fullerian professor of chemistry at the Royal Institution. Here he delivered eleven courses of day lectures, including three of the Christmas courses of juvenile lectures, originally initiated by Faraday. One of his Christmas courses was published as a book, entitled, "The Chemical Changes of Carbon." He also gave twenty Friday evening discourses, six of them before he became Fullerian professor. He resigned the chair in 1873. His book on "Animal Chemistry," published in 1866, is the substance of a course of lectures given at the Royal College of Physicians. His "Outlines of Chemistry," published in 1870, is a book written in the form of lecture notes without the use anywhere of a principal verb. It is a mine of useful chemical information.

In 1872 Odling succeeded Brodie as Waynflete professor of chemistry at Oxford. In the same year he married Elizabeth Mary, daughter of Alfred Smee, well known as the inventor in 1840 of "a new chemico-mechanical battery." Smee was an active investigator in other scientific subjects. His work on the potato disease brought him also into public prominence, with the inevitable result of much opposition and some satire.

"*Showman.* This is the aphis vastator, as you may see,
Very much magnified by Mr. Smee.
Boy. Please, sir, which is the aphis and which the tater?
Showman. Whichever you like, my young investigator."

Smee was also the author of the book "My Garden" (his garden at Carshalton). The Odlings' garden at Oxford was planned by him. He died in 1877, and his life, written by his daughter, Mrs. Odling, was published in the following year. Mrs. Odling died two years before her husband. There are three sons: George, who succeeded to his grandfather's property, and took the name of Odling-Smee; William, who joined the Army at the time of the Boer War and became Major in the Middlesex Regiment, serving as Lieut.-Colonel in the late war; and Marmaduke, who was a demonstrator at Leeds University and at present is chemist in an iron works at Middlesbrough.

In the early days of his Oxford professorship, Odling was elected President of the Chemical Society, succeeding Frankland in 1873 and being himself succeeded by Abel in 1875. He had been Secretary, 1856—1869, and Vice-President, 1869—1873. He was thus a member of the Council without a break for sixty-five years.

Odling found at Oxford his former co-secretary at the Chemical Society, Vernon Harcourt, who was Lee's Reader of Chemistry at Christ Church; W. W. Fisher was Aldrichian demonstrator of Chemistry; and Odling brought with him his assistant at the Royal Institution, Dr. John Watts, who has met with a remarkable success at Oxford as a college tutor. At first there was only one University laboratory, with accommodation for sixteen to twenty students. In 1879 a large new building was completed, the main part of which was fitted up at once, and the rest as occasion required. In 1902 there was a further building extension; so in thirty years' time there was accommodation for one hundred and twenty to one hundred and fifty students, besides private research laboratories. The time was the full tide of the Examination era; when some universities existed only to examine; when many universities and university colleges published their examination papers in their calendars; as much as to say: "This is the main business of our professors." Odling never

seemed fully to appreciate the high value and dignity of honours by examination. "I do not lecture for the examinations," he said. He prepared his lectures with much care, and it was his practice to have a printed syllabus of each term's course, sometimes a very full syllabus extending to more than thirty pages, in the style of his "Outlines of Chemistry." It is doubtful if he ever repeated a course. He was asked once to repeat a course he had given some time before, but he refused. The writer had the experience of attending the lectures of Odling and of Kekulé in the same year. With points of difference, they were alike in their unassuming authority. There was nothing second-hand; they were the lectures of men who had been at the making of the science they taught. Odling was never the slave of his laboratory. Even in early life his taste was for the philosophic and speculative rather than for the practical side of the science. Instead of directing the research work of his assistants and students, he preferred to let them work out their own ideas, and he held that the "best of all endowments for research is that with which the searcher, relying on his own energies, succeeds in endowing himself;" while he probably had little taste for research of the more stereotyped and made-to-order kind, he retained his keenness for new discoveries and new ideas. He showed the same enthusiasm for the new discoveries of Ramsay and the new ideas of van't Hoff that he had shown in his youth for Graham and for Laurent. He took an active part in the affairs of the University, and for fifteen years, from 1893 to 1908, was a member of the Hebdomadal Council. He was for a time President of the Ashmolean Society, and he lectured to the junior scientific and chemical clubs. He also took an interest in the extension movement and gave the inaugural lecture at the summer meeting in 1894. In 1882 his "Chemistry" primer was published. As it dealt with only a small section of the subject, it was possible to treat that section with some degree of fulness. One may say that it might have been written one hundred years earlier, and that it will not be out of date one hundred years hence.

Odling was the third President (1883–1888) of the Institute of Chemistry, which was founded in 1877. It was during Odling's presidency that the Institute obtained its charter. In 1907, on its thirtieth anniversary, the then President, Professor P. F. Frankland, said: "The leaders who guided the destinies of the Institute at its inception were not men to be easily baffled by opposition, and in eight years from the time of our foundation they succeeded in obtaining for us the Royal Charter which has been a pillar of strength ever since. But for this, the most memorable achievement in our annals, the whole profession of chemistry owes a deep and permanent

debt of gratitude to our then President, Dr. Odling, that veteran of British science whose fame as a chemical investigator began more than half a century ago."

Odling delighted in offering hospitality, and always had a welcome for his friends when they came to see him. But he was severely "not at home" to letters. On the writer asking for letters of scientific interest, he was informed that there were a great many letters, mostly from people asking for a reply to a previous communication. In one batch there were a number of letters unopened, ending with a prepaid telegram also unopened, all from the same source, and all carefully preserved. A friend of his says: "I wanted a reply from Odling on a matter which, at the time, I thought important. Letters had been of no avail. At his house I was told he had gone to Bournemouth. So I took a return ticket and the next train to Bournemouth. Mrs. Odling, who evidently knew why I had come, was inclined to be apologetic. Not so the professor. He was delighted to see me, took it as the most natural thing in the world that I should come to Bournemouth to see him, invited me to lunch and all that, and settled my business in a few minutes. I thought the whole thing was worth the expense; a prepaid telegram would evidently not have been. I also thought it was a gentle and effective way of hinting that the man of fussiness is not necessarily the man of business."

Odling was interested in literature, in art, and in the drama. He had a fine collection of engravings. In his youth he had many friends among actors. He was a member of the Garrick Club as well as of the Athenæum. When he was eighty he began to learn Spanish and attended a congress at Madrid, and was elected an honorary member of the Spanish Physical and Chemical Society. As early as 1875 the honorary degree of *Ph.D.* was conferred on him by the University of Leyden.

Odling was more than fifty before the writer of this memoir came to know him. Some friends of his who have known him longer have been good enough to contribute some personal memories of him for this memoir.

Sir William Tilden writes: "Probably no one who was not present at the meetings of the Chemical Society during some of the years when Odling was secretary can appreciate at their true value the services rendered by him to the progress of chemical theory in England. It is mainly due to his activity and clear vision that, in spite of the general sluggishness of chemical opinion at that time, the reforms introduced by Gerhardt, and especially by Cannizzaro, were accepted by his contemporaries. I was then working in Stenhouse's private research laboratory, where the isolation of

vegetable principles was the prime business, without reference to theory of any kind, and where any disturbance of the long-established Berzelian system of atomic weights and notation was viewed with an unfriendly eye. Stenhouse even went so far as to caution me against Odling's new manual, of which Part I only appeared in 1861, the author of which he denounced as 'a fantastical chap.' But this can only be received as an indication of Odling's influence, which is further proved by the fact that the book was soon afterwards translated into German. Part II never appeared.

"An acknowledgment by the Chemical Society is found in the fact that Odling was chosen at the Jubilee in 1891 to give the history of the changes in theory since the foundation of the Society.

"It is remarkable that Odling, with his powerful grasp of principles, did so little in the way of experiments. Like some other men of strong individuality, he probably preferred dealing with men and affairs to the patient pursuit of detail in experimental inquiry. If that is true, it was all the more remarkable that he should have chosen for investigation such a subject as the platinum bases, when he found himself in the laboratory of the Royal Institution. This did not carry him very far, and only one Friday evening discourse on the subject was given, in June, 1870. The report of this affords a characteristic example of his style.

"Frequenting the meetings, as I did, of the Chemical Society from 1863 onwards, I can recall the figure of Odling in those days as that of a smart, bustling young man, usually arrayed in a close-buttoned frock coat, showing a white waistcoat beneath, in some contrast to the rather slovenly figures of some of his contemporaries —Hofmann, for example. His precocity is referred to in Field's rhymes * ("*A Chemical Review*," by A. B., 1863). He became a Fellow of the Society in 1848, when he was but nineteen years of

* Sir William Tilden must refer to the following lines :—

"Odling well-known since boyhood's merry hours
. . . .
And I return, and find the quondam lad
Hath sprung to fame, and carrying on like mad;
A Guy's professor M.B., nothing less
Our secretary, and an F.R.S.
Writing a work symbolical and quaint
With names to tease the patience of a saint."

or this, in 1867 :—

"And Odling comes next so forensic and bold,
With a visage as fair and as fresh as of old;
Though he looks so good-natured, I think he can rule
The noisy recruits in Bartholomew's School."

age, and merely a medical student. But so early as 1856 he became one of the two secretaries, being associated apparently by way of contrast with Professor Theophilus Redwood, who at the meetings sat 'with stolid look and philosophic mien,' but never uttered a word."

Mr. H. T. Gerrans, Senior Fellow of Worcester College, writes:—

"On June 18th, 1872, Dr. Odling was elected to a Fellowship at Worcester College, Oxford, which he held throughout the tenure of his professorship, and on his resignation of the latter he was elected Honorary Fellow of the College.

"Under the Ordinance of the Oxford Commissioners which was in force in 1872, the Provost and Fellows were empowered to elect to a Fellowship the holder of a University professorship, and the mention to intending candidates for the chair of the probability of their taking action under this Ordinance was authorised by the governing body.

"It has been the custom of the college to hold annually two Stated General Meetings, to which non-resident Fellows were summoned, and, much more frequently and whenever necessary, meetings of resident Fellows for the transaction of the less formal business of the College. Dr. Odling was a regular attendant at Stated Meetings, and his assistance and advice were greatly valued. To the other meetings, although he resided in Oxford, he was not summoned unless matters of importance were under discussion.

"He was on the best of terms with his colleagues, and the present writer can record numerous acts of kindness. On occasions when there was a difference of opinion on college policy, Dr. Odling took great pains to acquaint himself with the views of both sides and endeavoured (often with marked success) to secure a working agreement.

"He had no share in the college teaching, but his invaluable advice on matters of art was always at our disposal."

Odling's original work in chemistry began at the close of one of the stormy times in the history of chemistry. The theory of compound radicals * (Lavoisier's radicaux hydrocarboneux et carbonhydreux), pushed to extreme limits by Berzelius, became unable to adapt itself to the discoveries of Dumas and Laurent in Substitution. The story has often been told, perhaps nowhere better than in the introduction to Kekulé's "Lehrbuch." The temper of the combatants was often short, and the language of some of them violent and not always polite. "Wenn Dumas erklären würde dass er den Wasserstoffgehalt in Chloral durch die Analyse und zwar mit Genauigkeit bestimmt habe so halte ich dies

* *I use the older spelling, which Odling himself strongly advocated.*

für Charlatanerie" (*Annalen*, 1840, **33**, 167). It is reassuring to learn that thirty years later Liebig and Dumas dined together amicably in Paris, although on opposite sides of the table. "Herr Gerhardt's Verfahren hat in den letzten Jahren auf mich immer den Eindruck eines Strassenräuber's gemacht" (*ibid.*, 1846, **57**, 117). "They called Gerhardt a brigand," said Odling, "and he certainly looked like one." "J'étais un imposteur, le digne associé d'un brigand, etc., et *tout cela pour un atome* de *chlor mis à la place* d'un atome d'hydrogène, pour une formule corrigée" (Laurent, "Methode de chimie," p. 248). Odling took the side of Laurent and Gerhardt. He translated Laurent's "Methode de Chimie," and published his first paper in the *Journal of the Chemical Society* in 1854. In this paper, "On the Constitution of Acids and Salts," the idea of valency as replaceable value of the atoms and radicals is introduced. Valency is represented by dashes thus: K′, Sn″, Bi‴, H′, O″, NO_2', SO_2''. He uses for valency the terms equivalency and replaceable, representative, or substitution value. He represented polybasic acids on the multiple water type by replacement of two or more hydrogen atoms by multivalent radicals, in particular phosphoric acid as derived from the triple water type $\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3$ by replacement of three hydrogen atoms by the triad radical PO‴, thus $\left.\begin{matrix}PO'''\\H_3\end{matrix}\right\}O_3$. Metaphosphoric acid he regarded as an anhydro-acid more complex than orthophosphoric, and related to it as a dichromate to a chromate; $PO'''\left.\begin{matrix}PO'''\\H_2\end{matrix}\right\}O_4$. He introduced the terms monad, dyad, triad, etc. The first two had been used by Laurent in a different sense. Laurent's monads and dyads Odling called artiads and perissads. He always insisted on the distinction between combining value and replaceable value, calling one 'desmicity' and the other 'adicity.' The first idea of valency is, however, older than Odling. It is found vaguely in Dalton's atoms and in the law of multiple proportions. It is definite enough in Graham's recognition of the first polybasic acid. Many others have developed it further. It still waits for final definition. Kekulé, who was in England at the time and published his first paper in the same year, says, "By means of a friend I became acquainted with Williamson. The theory of polybasic radicals was being developed. With Williamson was also associated Odling. It was an excellent school to encourage independent thought." Odling's paper on "The Constitution of Hydrocarbons" was the subject of his first lecture at the Royal Institution (*R. I. Proc.*, Vol. II). He accepts the radicals as convenient groupings, but not as definite

entities. Instead of a single radical for each substance, he admits as many radicals as possible. Thus he regards marsh gas as hydride of methyl, $H \cdot CH_3$, dihydride of methylene, $H_2 \cdot CH_2$, trihydride of formyl, $H_3 \cdot CH$, and tetrahydride of carbon, $H_4 \cdot C$. He gives a final complete form to the type theory by adding the fourth, or marsh gas, type to the other three—HCl, H_2O, H_3N, H_4C. Of the series of lectures instituted by the Chemical Society in 1854, Odling gave the seventeenth in 1858. It was on the "Atomic Weights of Oxygen and Water," and was the first of the series to be published. In it he gives convincing reasons for the atomic weight $O = 16$ and for the molecule H_2O instead of $O = 8$ and HO or H_2O_2, as generally in use at that time. These reasons he further developed in his "Manual of Chemistry," published in 1861. In the Manual he also gave O_3 as the molecular formula of ozone. The foundation for this was perhaps a little slender at the time, but his view was amply supported by the later work of Soret and of Brodie. In the Manual he adopted the plan of treating chemistry as a whole without subdividing it into organic and inorganic. The Manual had one defect in missing the Cannizzaro revision (Odling was not at first convinced by Cannizzaro). Consequently, while the atomic weights of the non-metals and of the perissad metals have their modern values, those of the dyad metals have only the half values. Possibly this is the reason why only Part I was published. Selections of Part II were published in the *Chemical News*, and a good deal still exists in manuscript. He received numerous congratulatory letters on the Manual, with some criticisms. Frankland wrote: "The chapter on general considerations pleases me exceedingly—still, I must join Brodie in his complaint about your new words." We have already had some of his new words—of some such as 'hygroscopicity,' 'dehydrateability' and the like, the meaning is obvious. Others, such as 'Klumene,' 'Xenoene,' 'Stylous' oxide, need explanation. Brodie wrote: "It seems to me by far the most scientific text-book we possess." And Wöhler: "Wertvoll und belehrend selbst für uns Alten durch die neuen Theorien und Grundsätze die darin klar und fasslich gegeben zu sein scheinen." Odling wrote several of the articles in Watts's Dictionary, which began to appear in the early 'sixties, in particular, those on "Atomic Weights" and on "Metals, Atomic Weights and Classification of," the former before and the latter after the Cannizzaro revision. He had fought hard and long for the atomic weight of oxygen, but chemists were slow to abandon the old system. Even Frankland was not yet (1861) convinced. He writes: "You have doubtless a balance of the argument on your side. Nevertheless, I hold that more than even a considerable

balance is necessary to justify a change in such an old-established thing as the atomic weight of oxygen." The doubling of the atomic weight of carbon was a necessary consequence. As late as 1893 the writer attended lectures in Paris of professors who still used the old atomic weights. The position and valency of aluminium then occupied Odling's attention. It had been grouped with iron. No compound was known which contained one atom of aluminium in the molecule. Hence its valency was doubtful. Odling, in conjunction with his brother-in-law, Buckton (*Proc. Roy. Soc.*, 1865), prepared aluminium ethide and methide and determined their vapour densities, in this way proving aluminium to be a triad. He proposed, therefore, to group aluminium with boron, and supported his proposal by general analogies, and the isomorphism of boracite, MgB_2O_4, with spinel, $MgAl_2O_4$. To the natural grouping of the elements, a subject on which he had written as early as 1857 (*Phil. Mag.*, **13**, 423), he gives a very definite form in 1864 (*Quart. J. Sci.*, **1**, 642). He arranges the whole of the elements into groups in the order of their atomic weights, with gaps for undiscovered elements (for example, gallium and germanium). In particular, he considers the differences between the atomic weights of analogous elements, and points out that those which have the greatest analogy have a nearly constant difference of 48 in their respective atomic weights. "Seeing," he says, "the large number of instances in which the atomic weights of proximate elements differ from one another by 48, or 44, or 40, or 16, we cannot help looking wistfully at the number 4 as embodying somehow or other the unit of a common difference."

Odling's classification of the silicates, begun in 1857, was elaborated in several papers. The experiments of York (*Phil. Trans.*, 1857) had shown a variable equivalent for silica with regard to the particular alkaline carbonate with which it reacted. Odling shows that this variability depends on the relative ease with which carbonic acid is expelled from the several alkaline carbonates. The silicates may be regarded as derived from an ortho-acid, H_4SiO_4, a meta-acid, H_2SiO_3, and a $\frac{3}{2}$- or para-acid, $H_6Si_2O_7$, somewhat analogous to the phosphoric acids. The alkaline silicates are, ortho Li_4SiO_4, meta K_2SiO_3, para $Na_6Si_2O_7$. In each class are found numerous examples among the silicates found in nature, for example, olivine, ortho Mg_2SiO_4; augite, meta $(CaMg)SiO_3$; serpentine, para $Mg_3Si_2O_7$. Ortho-acids he derived from the hydrides, HCl, $HClO_4$; H_2S, H_2SO_4; H_3P, H_3PO_4; H_4Si; H_4SiO_4; a view which he defended experimentally by the direct oxidation of HCl to, in the first instance, $HClO$, the subsequent conversion to $HClO_4$ being brought about by the action of heat. Meta- and

para-acids are derived from the ortho, either by loss of water or by addition of anhydride. His views on the platinum ammonia compounds were based on an ingenious but somewhat distant analogy. They were given in the *Philosophical Magazine*, 1869, in a lecture at the Royal Institution, and in the "Outlines." He compares ammonia to methylene, and metal ammonias to methylene and condensed methylene compounds as expressed by the following formulæ:

CH_2, methylene;	NH_3, ammonia.
$HClCH_2$, methyl chloride;	$HCl{\cdot}NH_3$, ammonium chloride.
$\begin{array}{l} Cl{\cdot}CH_2 \\ \quad\vert \\ H{\cdot}CH_2 \end{array}$	$\begin{array}{l} Cl{\cdot}NH_3 \\ \quad\vert \\ Ag{\cdot}NH_3 \end{array}$

Similarly, copper ammonium chloride, $CuCl_2,6NH_3$, and calcium ammonium chloride, $CaCl_2,8NH_3$, correspond with propyl chloride and butyl chloride respectively. There are also several papers on notation and classification, in particular on the classification of the paraffin hydrocarbons. Odling was sometimes a little casual in the publication of his ideas. Thus the marsh-gas type is given in a lecture, the constitution of ozone in the "*Manual*," and the constitution of bleaching powder, $Ca{<}^{Cl}_{OCl}$, in the "Outlines."

Odling retired from the professorship at Oxford in 1912. In the first year of his retirement he seemed somewhat restless. Then he settled down to write another book, and that on a subject which rather surprised his family and friends. It was called "The Technic of Versification." To the mere chemist it appears like a kind of type theory of verse with a symbolic notation, almost chemical. It was written in his favourite style without the use of any principal verb. It contains a fine anthology of English poetry. There is no incongruity here, that poetry should appeal to a man of science. Is not Discovery the poetry of Science? The book was dedicated to his wife. He died two years after her, on February 17th, 1921. His friends will think of him, in Gerhardt's happy phrase, as "l'ami Odling,"—and they will miss him.

J. E. MARSH.

PERCIVAL SPENCER UMFREVILLE PICKERING.

BORN 1858; DIED DECEMBER 5TH, 1920.

BY the death of Spencer Pickering on the night of Sunday, December 5th, 1920, science loses a man of keen critical ability, able to think independently of current dogma, and fearless in accepting the conclusions which he drew from experiment.

Pickering was born in 1858, the son of Percival A. Pickering, Q.C., and Anna Maria, daughter of John Spencer Stanhope and granddaughter of the famous Coke of Norfolk, Earl of Leicester. Pickering was proud of his family and spent much time in writing their records and tracing their connexions and relationships. He inherited from his father ample private means and throughout his life remained outside professional chemistry: he took only one appointment—that of Lecturer in Chemistry at Bedford College—and did not retain that for long.

He was educated at Eton and entered Balliol on January 19th, 1877. He became Brackenbury Natural Science Scholar; took Responsions in Michaelmas Term, 1877; "Pass Mods," in 1878, and both the "Preliminary Examination" and the "Final Honours" in Natural Science in Michaelmas Term, 1879—a not unusual procedure among the better men of that time. He went down after the Lent Term, 1880.

His independent spirit showed itself in a series of papers which he sent to the Chemical Society in his early student days: his first paper in 1878 on the reaction between sulphuric acid and copper, in which he declined to accept the current explanation, and his second, *horribile dictu,* controverting a paper recently published by his tutor, W. W. Fisher, on the interaction between manganese dioxide and hydrochloric acid, and showing with all the assurance of youth that the statements of fact in Fisher's paper were wrong, and that, even had they been correct, they would not have justified the conclusions drawn. After leaving Oxford Pickering set up a laboratory in his mother's house at Bryanstone Square, where he further investigated some of the inorganic substances he had studied at Oxford—manganese dioxide, copper sulphide, aluminium sulphate, etc.

He was, however, now beginning more serious work, and he studied the physical properties of solutions of acids, alkalis, and of certain salts, plotting the results and drawing conclusions as to the behaviour of the dissolved substance in the solution. He began a study of the heats of hydration of salts and followed this up with an investigation of the heat of dissolution of salts and the thermal phenomena of neutralisation. He was early led to the view that solution was not a purely physical process as had been supposed, but was the result of "residual affinity" of salts in virtue of which combination was possible with molecules of water. This view was published in 1885 and developed in 1887 (T., 1887, 51, 593), and in subsequent papers before the Chemical Society. In his own words: "Atoms in combining do not, in most cases, entirely saturate each other, but the molecules formed

exhibit a certain residual affinity capable of being saturated with other molecules. *The atom possessing the smaller valency is not (necessarily) entirely saturated by that possessing the higher valency. It is due to the residual affinity of either the non-metallic or metallic radicle in a salt molecule, and not to that of both radicles,* that water becomes attached to the salt."

Other physical measurements followed; density, electricity, conductivity, heat capacity, expansion by heat, freezing point of solutions of various concentrations; these were dealt with in a long and elaborate paper in 1890 (T., 1890, **57**, 64).

An inspection of the experimental curves brought out little: the first differentials were therefore calculated and then the second; these were found to lie on intersecting straight lines, and, no matter what property was under investigation, the changes occurred at the same points. Moreover, these points corresponded to definite simple hydrates. It was recognised that the method required figures of a high order of accuracy, but Pickering believed that he had attained this, and worked out his data to four or five decimal places; for example, among the heats of evolution on mixing sulphuric acid with water he gave $(t^1 - t)^{\circ}$ as 0·2628. Subsequently he claimed to have prepared some of the hydrates indicated by the breaks.

These views seemed entirely opposed to those put forward by Arrhenius in 1888, according to which dissolved electrolytes dissociate in solution. A considerable controversy arose which is ably summarised by the protagonists themselves in Watt's "Dictionary of Chemistry" (1894), under the heading "Solutions," Arrhenius and Pickering each contributing accounts of their own views. On reading these articles to-day the differences seem less than they probably appeared at the time. Arrhenius admitted that his hypothesis held only for dilute solutions and that concentrated aqueous solutions gave greater values than be expected, to explain which he assumed an attraction between the water and the dissolved substance. Pickering admitted that his experiments were confined to concentrated solutions, but argued that hydrates continue to exist when such solutions are diluted. He further maintained that the molecule of dissolved substance being thus combined with a large number of molecules of water would be equally attracted in every direction, and, as the magnitude of the force exerted by each individual water molecule must be small, it would move easily in any direction and act as if it were in the gaseous state. Finally, if the residual affinity of the atoms were great, the interaction with the solvent molecules would be proportionally great and the amount of affinity utilised in holding them

together might equal that utilised in attaching them to the solvent molecules, in which case there would be an equal distribution of affinity changes over the atoms, which could then move in any direction. There seems here a sufficient basis for compromise, but Pickering was never the man to deviate from a conclusion drawn from experiments, and he resolutely insisted on the fundamental nature of the difference between the chemical and the physical schools.

In 1890 he had been elected into the Royal Society, and he continued publishing papers on the hydrate hypothesis of solution until 1896, by which time nearly 100 papers had appeared.

But Pickering's interests were by no means confined to physical chemistry. Soon after he left Oxford, and during the whole of the time when these investigations were proceeding, he made weekly visits to Harpenden, which, although only a village, was already a place of scientific associations, having among its inhabitants no fewer than four Fellows of the Royal Society—J. B. Lawes, J. H. Gilbert, Robert Warington, and Richard Lydekker. It is stated that he came for the sake of his health; he had lost the sight of one eye while yet at school through injury by broken glass as the result of an explosion, and a second accident to the same eye five years later (in 1878) caused by a tennis ball, necessitated its removal; as a result he was not very robust in health; but it seems to have been more than valetudinarian considerations that impelled his weekly visits to Harpenden. When he came to the village he did not live in the grand style, but worked in the fields as a labourer among the labourers, drawing and spreading manure and shrinking from none of the tasks that they were required to perform. It was the time of William Morris and of Toynbee, and Pickering was essentially a man to prove all things by direct personal trial. In 1885 he bought a house in Harpenden and spent more and more of his time there, until in 1902 he gave up his London house altogether.

After 1896 Pickering ceased publishing papers for more than ten years, but he was not idle. His interests were changing. In 1894, in conjunction with the Duke of Bedford—an old school and college friend—he laid out a field at Woburn as an experimental fruit farm, to do for fruit what Lawes and Gilbert had done for agricultural crops. But although the work was different the spirit was the same: no matter how widely recognised a practice, or how heavily supported by authority, he would boldly challenge it by making the direct experimental test. Such a man could not expect to be popular with the pundits. Their attitude was well—albeit unconsciously—expressed by an expert writing in a

horticultural journal when the farm was closed after twenty-six years of solid work: Whilo regretting the cause, the ill-health of Mr. Pickering—the writer was "on the whole glad that the farm was closed." But while Pickering lived he mercilessly tested accepted dogma and thoroughly enjoyed the discomfiture of the "experts" when fruit trees planted wrongly, manured wrongly, and managed wrongly, nevertheless made better growth and produced better crops than the controls treated on conventional lines in accordance with accepted practice. In spite of the care taken in the experiments, the practical value of the work undoubtedly suffered from the fact that the conditions of soil and climate at Woburn differ from those of the typical fruit areas, whilst in the early days the management of the trees was not beyond reproach. Some of the more important experiments are now being repeated under more normal conditions at the Long Ashton Research Station. No fewer than seventeen Reports were published by Pickering and the Duke of Bedford, and the 18th Report is about to be issued. The results were summarised in 1919 in Pickering's book, "Science and Fruit Growing."

Perhaps his most important work from the physiological point of view was concerned with the mutual effects of one growing crop upon another. This arose out of an observation at Woburn that the effect of growing grass round apple trees is to arrest all healthy growth and absolutely to stunt the tree. The effect might have been due to various causes—changes in aeration, temperature, water supply, food supply, or physical condition of the soil, but careful experiments failed to show that any of these factors came into play. Further experiments indicated that plant roots gave off something toxic to other plants. Pickering made efforts, but without success, to isolate the substance and concluded that it was very unstable, easily oxidising to produce another substance beneficial to plant growth. Other experiments brought out certain remarkable differences between vegetative growth and fruiting which are not yet explained: he found, for example, that manures were almost ineffective on fruit trees, although they behaved to bush fruit as to agricultural crops. Detailed studies were made of several of the more important washes and sprays—including Bordeaux mixture—which were removed from the realm of empiricism and put on a sound chemical basis. This work brought him once more into pure chemistry, and in 1907 he began publishing papers on the basic and complex salts obtained during the fungicide investigations. The soil work then beginning at Rothamsted attracted him and he carried out interesting and suggestive work on the action of heat and antiseptics on soils and on flocculation.

In the 1890 paper there is a little touch that reveals the whole man. Amid the austere array of figures and deductions there is a flash of romance that would not be subdued—a graceful reference to the patience and accuracy of "a little girl who had devoted all her spare time to the laborious calculations involved in the present work." Seven years later the "little girl" became his wife and for twenty-three years thereafter his inseparable companion. As in his papers so throughout his life, and even at the end, the vein of romance would peep out in spite of rigid self-repression; it revealed itself in his taste in art, in music, in literature, and in his last request to be buried in a rock at Woollacombe in the path of the sun, overlooking the western sea.

But his love of science never faltered: he had no children, and, subject to his wife's life-interest, leaves the bulk of his fortune to the Royal Society for the promotion of science, especially those branches that had interested him.

E. J. R.

JOHN SHIELDS.

BORN MAY 24TH, 1869; DIED OCTOBER 31ST, 1920.

JOHN SHIELDS, the son of a prosperous farmer of the Lothians, was born near Bathgate on May 24th, 1869. He received his elementary education at Bathgate Academy and at Daniel Stewart's College, Edinburgh. At the age of seventeen he entered the University of Edinburgh as a science student, and it is at this period that the present writer, who was then a demonstrator in the Chemistry Department, first made his acquaintance. Shields was a tall youth with a country freshness about him, keen on his work, and of an intense seriousness—broken by flashes of a dry, pawky humour. His mode of work at that time gave little promise of the neatness and exactness of manipulation which characterised him later: his bench was constantly swimming with reagents, but yet he had the knack of always getting accurate results. He graduated as B.Sc. in Chemistry and Physics in 1889, and then proceeded to Strassburg, studying under Fittig and Kohlrausch, and receiving the degree of Ph.D. in 1890 for a thesis on "The Reduction of Phenylparaconic Acid and Phenylbutyrolactone." The "Joseph Black" prize was awarded to him by the University of Edinburgh in the same year for an essay on "Condensation." On his return to Edinburgh in 1891 he gained the Hope Chemistry Prize and an 1851 Exhibition Scholarship. The winter of 1891—

1892 he spent in Leipzig under Ostwald, and the following summer with Arrhenius in Stockholm, where he carried out a fundamental research on the extent of hydrolysis in aqueous solutions of salts of weak acids. The second year of his scholarship was passed in University College, London. He there collaborated with Ramsay in the well-known investigation of the molecular weights of liquids by the method of surface-tension. A pair of co-workers better matched in diversity could not well be imagined. To those privileged to watch the progress of the investigation it was a source of unfailing enjoyment to see the clash of temperaments of these two Scots—Ramsay, burning with *perfervidum ingenium*, impatient for more and ever more results; Shields, calm, cautious, critical, never quite convinced that that last capillary was *really* clean, insisting on repetition and the utmost attainable accuracy. A reference to the original paper will show how well the collaboration succeeded.

Towards the end of 1893 Shields entered the service of Ludwig Mond, and during the succeeding five years carried out for him researches in pure science and in technology, amongst those published being important investigations on the absorption of hydrogen by platinum and by palladium. The next three years Shields spent at Leven, Fifeshire, as technical adviser and works chemist to the Scottish Cyanide Company. This company was working a process for the production of cyanide by the fixation of atmospheric nitrogen, but found difficulty in manufacturing a marketable product. Under the advice of Shields the process and plant were remodelled and a satisfactory cyanide was at length obtained, too late, however, to save the company financially, as the South African War had for the time practically ruined the cyanide market. Shields thereupon renewed his relations with Mond, and for the next two years executed in his service special technical researches.

In 1903 he was appointed Chemical Engineer to the Rio Tinto Company, his work being at first of an advisory nature in London; but after a few years he became Chief Chemical and Metallurgical Engineer at the mines near Huelva, spending part of the year in Spain and part at home. He was responsible for all the processes connected with the treatment of pyrites and its products, including the production of sulphuric acid and superphosphate as well as the copper extraction; he supervised the research work connected directly and indirectly with these processes, and designed and constructed plant embodying the results of his discoveries and inventions. About Christmas 1919 Shields resigned his position with the company and returned to London. It was his intention to take up fresh work, but towards the middle of 1920 he showed

signs of failing health. In August, Shields, who was always a keen sportsman, caught a chill while shooting in Scotland, and gradually developed an illness which culminated in his death of bronchial pneumonia on October 31st at his home in London.

Shields was a practical man through and through, and was possessed of rare constructive and manipulative skill: the theoretical aspect of chemistry interested him but little, save in so far as it guided and influenced practice. He was a genial companion and an interesting talker, especially on the subject of his Spanish experiences. Indeed, he seemed to have acquired during his stay in Spain something of the atmosphere of the country, his strikingly picturesque appearance in later years giving more than a suggestion of the Spanish hidalgo.

Shields married, in 1895, Miss Jane H. G. Murray, daughter of Mr. J. L. Murray of Heavyside, Biggar. He is survived by her and by two married daughters. J. W.

LEONARD PHILIP WILSON.

Born 1879; Died October 16th, 1920.

A regrettable consequence of the choice of an industrial career by the young chemist is that henceforth his doings are largely hidden from the chemical world; for this reason probably few realise how great a gap the early death of L. P. Wilson has left in our ranks. His achievements and knowledge entitle him to a place in the very first rank amongst British industrial chemists of his own age, although a certain modesty, amounting almost to shyness in public, prevented his accomplishments from becoming widely known.

The precise part his work played in the wonderful achievements of the artificial silk industry is, of course, known only to Messrs. Courtaulds, but it is understood to have been not inconsiderable: throughout his career he showed marked originality.

Wilson was educated at St. Dunstan's College, Catford, and thus early came under the inspiration of C. M. Stuart, himself a chemist of no mean ability, and a most capable teacher. The positions taken in the chemical world by W. A. Davis, C. S. Gilles, L. P. Wilson, E. F. and H. L. Armstrong, C. E. Mees, E. Sheppard, L. W. G. Brooker, G. Rudorf, and C. J. Regan, to mention only a few, afford sufficient testimony of the influence which a scientifically trained man of high ideals can exercise in our public schools.

Proceeding to the Central Technical College in 1896, Wilson headed the list at the entrance examination, gaining the Clothworkers' Company's Scholarship; he was awarded the diploma of Associate in 1899. For a year he held the Leathersellers' Research Fellowship at the Central Technical College, being engaged in the study of acetanilide, and other anilides which were expected to exhibit isomorphous relationships. This work was undertaken largely as a preliminary to the separation of the isomorphous derivatives of the rare earths.

At the Central Technical College Wilson received a thorough training in the elements of Engineering and of Electrical practice, in addition to Chemistry: the value of this to him is evidenced by the very practical nature of the inventions he subsequently made.

Wishing to follow an industrial career, he entered the services of Messrs. Wilkinson, Heywood & Clark, Limited, the well-known paint and varnish makers, working first at their Poplar and subsequently at their West Drayton works. He originated several new and successful processes for the refining of oil, purification of turpentine, etc. He left them in 1905, and after a short term with the Vacuum Oil Co. of Birkenhead—where he studied the manufacture of solid lubricants—became, in 1906, chemist to Messrs. S. Courtauld & Co. of Coventry, who had then recently commenced the manufacture of artificial silk by the viscose process: cellulose in the form of wood pulp is treated with sodium hydroxide and carbon disulphide to form a soluble compound, the solution of which is then squirted into a coagulating bath, forming filaments from which lustrous threads of cellulose are obtained after washing, drying, bleaching, etc.

In 1917 Wilson was promoted to be chief Chemist at Coventry, the firm—now Messrs. Courtaulds, Limited—having in the meantime achieved world-wide repute for the production of an article but little inferior to natural silk.

His first patent, taken out in 1908, deals with the use of glucose or other sugar together with a mineral acid, as an addition to the coagulating bath in the preparation of artificial threads from viscose: this invention is generally understood to have had a far-reaching effect in the development of the viscose process.

In conjunction with W. H. Glover, another old Centralian, Wilson worked out and patented in 1914 and 1915 the process of maturing mercerised cellulose by treatment with an oxidising agent such as a soluble peroxide, a hypochlorite, or a current of oxygen in presence of a metallic catalyst: this process has now become an essential feature in the viscose process.

About the same time he patented a process for the manufacture of tubular threads, and another for the regeneration of the polysulphides obtained in the desulphurising of viscose.

In 1917 he contributed a full and authoritative account of the artificial silk industry to the *Journal of the Society of Chemical Industry*, and brought this up-to-date in 1920. These papers give a most comprehensive outline of the manufacture of artificial silk and evidence the amount of chemical work involved in its development. Probably the artificial silk industry has helped as much directly and indirectly to increase the knowledge of cellulose as have the other great industries of cotton, paper, and explosives, which depend on this raw material.

Perhaps Wilson's most important contribution to science is that published jointly with Miss Imison just after his death: it will undoubtedly have an important bearing on the future theory of dyeing. Methods having been devised to measure the extent to which a dyestuff can exhibit unevenness in dyeing artificial silk, a large number of substantive dyes were examined and classified. It was found that evenness varies according to the molecular weight of the dye used, the arrangement of the groups in the molecule having no real effect. Fabrics made of artificial silk of varying affinities will show variations in shade when dyed with dyestuffs of high molecular weight, and a practically even effect if dyestuffs of low molecular weight are employed.

In recognition of his valuable contribution to the artificial silk industry, Wilson received the Fellowship of the City and Guilds Institute in 1911; he became a Fellow of the Institute of Chemistry in 1918. He took a strong interest in the Society of Chemical Industry and was Chairman of the Birmingham Section in 1919—1920 and a Vice-President of the Society at the time of his death. His knowledge of patent law made him a valuable member of the Patents Committee of the Association of British Chemical Manufacturers.

E. F. A.

LXIII.—*The Influence of Salts on Chemical Equilibria in Solutions.*

By J. N. Brönsted.

1. *Introduction.*

Most equilibria into which salts enter in aqueous solution are not distinguished by real constancy of the equilibrium "constant," such as is the case with equilibria between neutral substances. The failure of previous attempts to account for this peculiarity of salt solutions is undoubtedly due to the fact that, directly or indirectly, the method of electric conductivity constituted the basis of the calculations of ionic concentrations, no regard having been taken to the interionic forces originating with the electric charges of the ions.

The difficulties which here and in many other fields the classical theory of salt solution encounters can be overcome in great measure by assuming that strong electrolytes are completely dissociated and that interionic forces are responsible for the abnormalities observed. From the point of view of this theory, which has recently been developed by several authors (Milner, *Phil. Mag.*, 1912, [vi], **23**, 553; 1913, [vi], **25**, 742; Bjerrum, *Zeitsch. Elektrochem.*, 1918, **24**, 321; Ghosh, T., 1918, **113**, 449, 627, 707), the writer has shown (*J. Amer. Chem. Soc.*, 1920, **42**, 761) that the problem of the simple solubility equilibrium can be successfully attacked. It is an obvious conclusion, therefore, that also in the case of more complicated equilibria, involving strong and weak electrolytes in a homogeneous phase, the introduction of the same points of view will enable outstanding anomalies to be removed.

In order to understand the influence of the addition of a salt on a system in chemical equilibrium we must consider the effect of it on any species of molecules or ions present, assuming that neither of them reacts chemically with the added salt. Now it is a well-known fact that the addition of a salt to a solution of a non-electrolyte usually causes the chemical potential or activity of such a substance to increase. This consequence appears most clearly in the solubilities of non-electrolytes, which exhibit—at least in the range of dilute solutions—an almost rectilinear fall with increasing concentration of the added salt. Since in the saturated solution the following thermodynamic equation holds good:

$$\xi = sf = \text{constant} \quad . \quad . \quad . \quad (1)$$

where ξ, f, and s indicate respectively activity, activity coefficient, and solubility of the dissolved non-electrolyte, a rectilinear increase of the activity coefficient, or of the activity in the case of constant concentration, follows.

Quite differently run the solubility curves in the case of a sparingly soluble salt as solute. If the salt is uni-univalent, the equation

$$\log s = \tfrac{1}{3}\sqrt[3]{c_t} + \text{constant}, \quad . \quad . \quad . \quad (2)$$

where s is the solubility and c_t the total ionic concentration of the solution, has been recently shown by the writer to apply approximately. Introducing in (2) the thermodynamic equation :

$$\xi'\xi'' = c^2f'f'' = \text{constant} \quad . \quad . \quad . \quad (3)$$

where ′ and ″ refer to each one of the two ions of the saturating salt, and assuming the activity coefficients of the ions to be equal and $= f$, we see this coefficient is determined by :

$$\log f = -\tfrac{1}{3}\sqrt[3]{c}\,. \quad . \quad . \quad . \quad (4)$$

an *expression which agrees fairly well with that given by Bjerrum.*

Also when ions of higher valency are considered, solubility measurements can be used to determine their activity coefficients. *A series of measurements made in this laboratory, particularly in* the group of the metal ammonia salts, shows that the increase in solubility caused by the addition of heteroionic salts is very pronouncedly *a function of the valency of the ions of the saturating* salt. This is shown in the following table containing the data for the bi-bivalent xanthocobaltic chromate and the ter-tervalent *luteocobaltic hexacyanocobaltiate in sodium chloride solutions at* 0°. S is the molal solnbility at the concentration c of the solvent, S_0 the solnbility in pure water.

TABLE I.

Solubility Ratio S/S_0 *of Xanthocobaltic Chromate* ($S_0 = 0{\cdot}000257$ *mol.*) *and Luteocobaltic Hexacyanocobaltiate* ($S_0 = 0{\cdot}000007$ *mol.*) *in Sodium Chloride Solutions at* 0°.

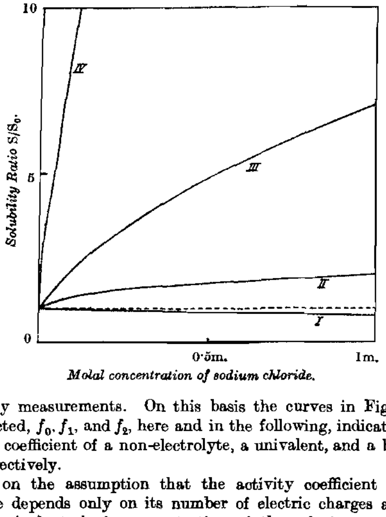
C.	Xanthocobaltic chromate.	Luteocobaltic hexacyanocobaltiate.
0	1·00	1·00
0·05	1·61	5·40
0·1	2·19	9·30
0·2	3·04	17·8
0·5	4·10	49·6

The extraordinarily increasing values of S/S_0 shown in this table allow us to infer that in the case of multivalent ions we have to do

with very high interionic forces. We obtain most clearly a survey of the influence of the electric charges when considering Fig. 1, in which the solubility ratio S/S_0 is plotted against the concentration *c of the solvent for the four cases of saturating substances dealt* with above. The curves I, II, III, and IV refer to uncharged molecules, uni-, bi-, and ter-valent ions respectively.

As in the case of uni-univalent salts, equation (3) will also enable us to calculate for salts of higher type the activity coefficients from

FIG. 1.



Molal concentration of sodium chloride.

solubility measurements. On this basis the curves in Fig. 2 are constructed, f_0, f_1, and f_2, here and in the following, indicating the activity coefficient of a non-electrolyte, a univalent, and a bivalent ion respectively.

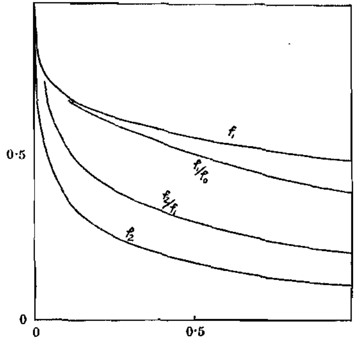
Now on the assumption that the activity coefficient of any molecule depends only on its number of electric charges and the total, equivalent, ionic concentration of the *solution concerned*, the results mentioned above give us a means of tracing the influence of salts upon the homogeneous, chemical equilibrium in any particular case. No regard, however, is taken in these calculations to the markedly individual behaviour of ions of identical types, and we have to realise therefore the approximate nature of the results arrived at on this assumption. As it is the purpose of the present article to state only the general principles of chemical equilibria in

salt solutions, consideration of these individualities, although of great importance, may be omitted for the present.

The numerical calculations of homogeneous equilibria stated in the following sections cannot therefore be looked upon as conclusive but only as yielding the average or approximate value of the salt effect in a system of the particular type considered.

On the other hand, as a conclusive result of the above interpretation of the salt effect, we are justified in maintaining the rigid

FIG. 2.



validity of the law of mass-action and of the gas laws in the case of equilibria established in relatively strong salt solutions of unchanged concentrations. This view has recently been fully verified by the writer in a number of instances (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 25. *K. Danske Vid. Selsk. math.-natur. v. Medd.*, 1920, **3**, No. 9).

2. *The Dissociation of Water and other Weak Electrolytes.*

From quite a different point of view from that given above Le Blanc (*Zeitsch. physikal. Chem.*, 1891, **8**, 314) already suspected the dissociation of water to be augmented by the addition of salts. The same conclusion was reached by von Euler (*ibid.*, 1899, **28**, 626) and Lewis and Wheeler (*ibid.*, 1906, **56**, 190) in the case of other dissociating substances on the ground that the dielectric constant of the solvent was increased by the addition of a salt.

The effects in question, however, are very slight as compared with the influence of the changing activity coefficient according to the assumptions underlying the present theory.

In a diluted, aqueous solution the water activity will be nearly constant, and therefore:

$$\xi_{H^{\cdot}} \cdot \xi_{OH'} = k^{\xi} \quad . \quad . \quad . \quad . \quad (5)$$

where ξ denotes activity and k_{ξ} is a constant which may be termed the thermodynamic dissociation constant. Introducing $\xi = cf$ and assuming the activity coefficient f to be the same for all uni-univalent ions present in the solution, we can write:

$$c_{H^{\cdot}} \cdot c_{OH'} = k_c = \frac{k_{\xi}}{f^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

which shows that the product of the concentrations of the hydrogen- and hydroxyl-ions—the usual dissociation constant k_c—is not a constant, but increases with increasing ionic concentration since the activity coefficient f decreases. Calculation according to (4) yields for the ratio of k_c at 0·01 and 0·1 normal solution:

$$\frac{(k_c)_{0\cdot 01}}{(k_c)_{0\cdot 1}} = 0\cdot 68,$$

whilst from the measurements of Löwenhertz (*Zeitsch. physikal. Chem.*, 1896, **20**, 291) of the acid-alkali cell at the same concentrations the number 0·71 can be calculated for this ratio, again with the assumption of equal activity coefficient at equal concentration. Not too much weight, however, should be attached to this agreement on account of the adherent uncertainty regarding the liquid junction potential in the experiments of Löwenhertz. For the same reason, most experiments on the acid–alkali cell communicated by other investigators (Poma and his co-workers, *Zeitsch. physikal. Chem.*, 1912, **79**, 55; 1914, **88**, 671*; Lorentz and his co-workers, *ibid.*, 1907, **60**, 422; 1909, **66**, 733; Harned, *J. Amer. Chem. Soc.*, 1915, **37**, 2460) can furnish no adequate verification of the theory advanced to account for the varying dissociation of water.

It follows from equations (5) and (6) that the hydrogen-ion potential can be expressed by

$$\pi = RT \log f_{H^{\cdot}} + \text{constant}$$

and

$$\pi = -RT \log f_{OH'} + \text{constant}$$

* The numerical calculations of the ratio of hydrogen-ion concentration are erroneous throughout this paper on account of the use of natural instead of common logarithms.

in solutions containing a strong acid and a strong base of constant concentration respectively. Addition of salts, therefore, will *influence the potential of the hydrogen electrode in opposite* directions in the two cases to an extent computable by equation (4). This conclusion, too, might easily be tested, sufficient means being provided for the elimination of the liquid junction potential.

Now, when considering a weak electrolyte dissolved in water, for example, a weak acid, dissociating according to the scheme :

$$AH \rightleftarrows A' + H^{\cdot}$$

it is evident from our theory that the addition of salts will increase the dissociation to a greater extent than in the case of water as the electrolyte. Whilst in both cases the activity coefficients of the ions are decreased, we have for the acid, in addition, an increase in activity of the undissociated molecules. When the acid is sufficiently weak an augmentation of its total activity must ensue.

The change in the ordinary mass-action constant k with change of concentration can be computed when in the thermodynamic expression :

$$\frac{\xi_{H^{\cdot}} \cdot \xi_{A'}}{\xi_{AH}} = \frac{c_{H^{\cdot}} \cdot c_{A'} f_{H^{\cdot}} \cdot f_{A'}}{c_{AH} f_{AH}} = k_{\xi} \quad . \quad . \quad . \quad (7)$$

the activity coefficients $f_{H^{\cdot}} = f_{A'} = f_1$ and $f_{AH} = f_0$ given in the foregoing section are introduced. Hence it follows that

$$\frac{c_{H^{\cdot}} \cdot c_{A'}}{c_{AH}} = k_c = k_{\xi} \frac{f_0}{f_1^2} \; . \quad . \quad . \quad . \quad (8)$$

An influence in this direction has already been assumed by Arrhenius in an important paper (*Zeitsch. physikal. Chem.*, 1899, **31**, 197) on the influence of salts on the velocity of inversion caused by weak acids. From experiments on this subject Arrhenius drew the general conclusion that the *addition of salts causes an increase* of the dissociation constant corresponding with the effect of increasing concentration in a pure solution of a strong electrolyte.

The present theory of the effect of the addition of salts, which in the case under consideration is indicated by equation (8), is compatible with the experimental results of Arrhenius. When the concentration of the weak acid is unchanged and the slighter influence of f_0 is disregarded, equation (8) requires approximate constancy of the product $c_{H^{\cdot}} \cdot f_1$. On the further assumption that the relative speed h of the reaction is directly proportional to the hydrogen-ion concentration, we find $hf_1 =$ constant. The figures in Table II prove this really to be the case.

TABLE II.

Relative Velocity h *and Acidity Coefficient* f_1 *in Mixtures of Acetic Acid* (0·025 *mol.*) *and Potassium Chloride* (c).

c.	*h.*	f_1.	hf_1.
0·125	1·354	0·682	0·92
0·05	1·205	0·752	0·91
0·02	1·135	0·809	0·92
0·0075	1·083	0·855	0·93

When comparing the figures given in the last column, however, *we must bear in mind that even in the case of strong acids a salt* exerts some influence on the velocity of reaction, the specific, catalytic action increasing slightly with the salt concentration. For this cause a change of 5 per cent. may occur in the values of hf_1. Nevertheless we are justified in concluding that an alteration of the dissociation of the weak acid in fairly good agreement with our calculations is indicated by these experiments.

From the same point of view we are able to account for the phenomena exhibited by *sparingly soluble, weak acids as saturating* substances in salt solutions. As was shown by Hoffmann and Langbeck (*Zeitsch. physikal. Chem.*, 1905, **51**, 385), salicylic acid and other weak acids show a maximum of solubility at a certain salt concentration. This result is explained by the fact that in dilute solutions the steeply decreasing course of the activity coefficient of the ions (f_1) must play the chief part in altering the activity of the acid, whilst at higher concentrations the change of f_0, owing to the salting-out of the undissociated portion of the acid on account of the slight dissociation, will be of greatest effect. Calculation of the experimental data shows a fairly close agreement with the requirements of the activity curves in Fig. 2.

It seems to the writer, therefore, that the theoretical reasons for the *assumption of increasing dissociation of a weak electrolyte on* the addition of salts, as well as the corroborating, experimental facts, are sufficiently conclusive to settle this question.

In some recent papers McBain and his co-workers (T., 1914, **105**, 1517; 1919, **115**, 1332) have advanced a conflicting opinion, based partly upon the theory developed by Goldschmidt, Snethlage, and others that the catalytic action of acids is due to the influence of the undissociated molecules as well as of the ions, partly upon the *argument that the increase in activity of the undissociated* molecules of the weak acid produced by the addition of salts is counterbalanced by an equal increase in the activity of the hydrogen ion, no displacement of the equilibrium therefore being bound to occur. The arguments of McBain, however, are not unassailable, because the theory of the catalytic influence of undissociated

molecules, as shown by Bjerrum, possesses very little probability, and the anomalies are much more simply explained by assuming a certain salt effect on the velocity of reaction analogous to the effect exerted by salts on the activity coefficients. It is true that the equilibrating increases in activity of acetic acid and its hydrogen ions have been ascertained approximately through the measurements of McBain and Walpole. This result, however, is a rigid requirement from the thermodynamic law of mass action, if we, with McBain, assume the activity of the acetic ion to be unchanged, and is therefore of no consequence for the question of change in the degree of dissociation. This question cannot be attacked thermodynamically without considering the activities as well as the activity coefficients of the molecules involved.

3. *The Equilibrium in Regulator Mixtures.*

The chemical systems to which the term "regulator mixture" is applied can be characterised by the following equilibrium scheme :

$$A \rightleftarrows B + C,$$

where one of the right-hand substances, for example B, is present in very small concentration as compared with the concentration of two other substances. The best known regulator mixtures are those in which B is the hydrogen- or hydroxyl-ion.

It will be useful to draw a distinction between acid and basic regulators. This distinction depends, not on the acid or alkaline reaction shown by the solution, but on the scheme of equilibrium belonging to the mixture, namely,

$$AH \rightleftarrows A' + H^{\cdot}$$

in the case of an acid regulator, for example, acetic acid + sodium acetate, and

$$BH^{\cdot} \rightleftarrows B + H^{\cdot}$$

in the case of a basic regulator such as ammonia + ammonium chloride.

In the first case the equation :

$$\frac{\xi_1}{\xi_0} = \frac{k_\xi}{\xi_{H^{\cdot}}} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

applies thermodynamically. From this we derive :

$$\log \frac{f_1}{f_0} = k_\xi + p_{H^{\cdot}} + \log \frac{c_0}{c_1} \quad . \quad . \quad . \quad (10)$$

where $p_{H^{\cdot}} = -\log H^{\cdot}$ according to Sörensen (*Medd. Carlsberg*

Lab., 1909, **8**, 1) is termed the hydrogen exponent. In the case of a basic regulator we have

$$\frac{\xi_1}{\xi_0} = k_\xi \, \xi_{H^\cdot} \quad . \quad . \quad . \quad . \quad (11)$$

and correspondingly

$$\log \frac{f_1}{f_0} = k_\xi - p_{H^\cdot} + \log \frac{c_0}{c_1} \quad . \quad . \quad (12)$$

Of course these equations also hold good in the case of solutions of pure weak acids or weak bases. They can be applied much more advantageously to regulator mixtures, however, because the ionic concentration c_1 is known here from the composition of the mixture, when the salts in this are considered to be completely dissociated. By measuring $p_{H^\cdot}$ electrometrically in the regulator mixtures at various concentrations, or when various amounts of salts are added, we are therefore enabled to calculate the corresponding changes in f_1/f_0 and thus to test the validity of the theory given in the first section. It is a point of importance for the application of formulæ (10) and (12) to such a system as a regulator mixture that the influence of the changing medium on the activity of the hydrogen ion manifests itself independently of the influence on its activity coefficient. On account of the very small hydrogen-ion concentration displacement of the equilibrium will cause no sensible changes in c_0 and c_1, the changes in f_0 and f_1 therefore affording the only causes for the measured alteration of $\xi_{H^\cdot}$.

Regulator mixtures of this kind have been very thoroughly investigated, especially by Sörensen and his pupils (*Medd. Carlsberg Lab.*, 1909, **8**, 1; 1910, **8**, 373; 1910, **9**, 10; 1911, **10**, 146). Valuable material for a verification of formulæ (10), (12) and (13) has thereby been obtained.

We shall first consider the *phosphate mixtures* produced by mixing 1/15 molal solutions of primary and secondary alkali phosphates. The equilibrium in these is represented by

$$H_2PO'_4 \rightleftarrows HPO''_4 + H^\cdot$$

and the corresponding equilibrium equation analogous to (10); therefore:

$$\log \frac{f_2}{f_1} = k_\xi + p_{H^\cdot} + \log \frac{c_1}{c_2} \quad . \quad . \quad (13)$$

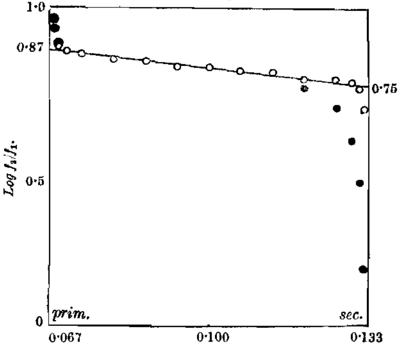
Sörensen's measurements of the ratios c_p/c_s in which the solutions of primary and secondary phosphates are mixed, the $p_{H^\cdot}$ found, and $\rho = \log f_2/f_1 + k$ calculated from (13), k being an arbitrary constant, are given in Table III.

TABLE III.

c_p/c_s.	p_{H}.	ρ.	c_p/c_s.	p_{H}.	ρ.
0·0101	8·68	0·683	1·500	6·643	0·819
0·0256	8·338	0·746	2·333	6·468	0·836
0·0526	8·043	0·764	4·0	6·239	0·841
0·111	7·731	0·777	9·0	5·906	0·860
0·250	7·381	0·779	19·0	5·589	0·868
0·429	7·168	0·800	39·0	5·288	0·879
0·667	6·979	0·803	99·0	4·944	0·940
1·000	6·813	0·813			

As seen from the figures in the last column, $\log f_2/f_1$ exhibits no constant value, but increases gradually as the solution changes from secondary to primary phosphate. This is explained by the fact that the equivalent concentration of the primary phosphate is only one-half of that of the secondary salt. The change is shown more clearly in the accompanying diagram (Fig. 3), where the equivalent

FIG. 3.



Equivalent concentrations of primary and secondary phosphates.

concentrations ranging from 0·067 to 0·133 are plotted as abscissæ and the values of $\log f_2/f_1$ in Table III are indicated by white circles. By means of a straight line drawn through these points a difference of 0·12 is found between the values of $\log f_2/f_1$ at pure primary and pure secondary salt, whilst the most fitting curve gives 0·10. Since the corresponding value taken from the curves in Fig. 2 is 0·09, we see that our theory accounts rather satisfactorily for the salt effect measured in this system.

The black points in Fig. 3 belong to a series of measurements in

which the specimen of secondary phosphate used contained a few units per cent. of the primary salt. The strongly diverging course exhibited by these measurements shows that such an impurity can easily be detected by means of calculations of this kind. A content of 2·6 per cent. of primary salt is conformably computed from the last three points.

Other regulator mixtures measured by Sörensen were glycine $+ 0{\cdot}1N$-hydrochloric acid and glycine $+ 0{\cdot}1N$-sodinm hydroxide, representing a basic and an acid regulator respectively. As the glycine solution was decinormal with respect to sodium chloride and no change in the salt concentration therefore occurred on mixing the solutions, a constant value of f_1/f_0 was expected to be calculated from equations (10) and (12). This was found to be the case when due regard was taken to the amount of hydrogen- and hydroxyl-ions in these mixtures, which was so great as to have a sensible influence on c_1.

In the case of borate and citrate regulators calculations of this kind meet with difficulties owing to the fact that no single equilibrium prevails in these mixtures. In mixtures of boric acid and alkali various condensed acids and ions are present, and in the case of citrate mixtures simultaneous equilibria between CiH_3, CiH'_2, CiH'', and Ci''' (where $Ci = C_6H_5O_7$) prevail in all ranges of mixtures used in the measurements.

In the foregoing measurements with phosphate mixtures the concentration changed only from 1/15 to 2/15. Pahitzsch has examined the same mixtures with the addition of sodium chloride, using a much wider range of total concentration. The results of his measurements are collected in Table IV.

TABLE IV.

	m.	c_{NaCl}.	c.	$p_{H^{\cdot}}$.	ρ_f.	ρ_c.
	1/150	0	0·0067	5·48	0·00	0·00
$c_p/c_s = 39$	1/60	0	0·0167	5·43	− 0·05	− 0·04
	1/15	0	0·067	5·29	− 0·19	− 0·14
	1/150	0·1	0·107	5·19	− 0·29	− 0·21
	1/150	0·25	0·257	5·03	− 0·45	− 0·34
	1/150	0·5	0·507	4·91	− 0·57	− 0·43
	1/60	0·5	0·517	4·85	− 0·63	− 0·44
	1/15	0·5	0·567	4·84	− 0·64	− 0·47
	1/15	0·7	0·767	4·74	− 0·74	− 0·54
	1/150	1·0	1·007	4·65	− 0·83	− 0·63
$c_p/c_s = 11{\cdot}5$	1/15	0	0·068	5·81	0·00	0·00
	1/15	0·5	0·568	5·35	− 0·46	− 0·33
	1/15	0·7	0·768	5·25	− 0·56	− 0·40
$c_p/c_s = 5{\cdot}67$	1/15	0·0	0·072	6·10	0·00	0·00
	1/15	0·5	0·572	5·67	− 0·43	− 0·33
	1/15	0·7	0·772	5·55	− 0·55	− 0·40

In this table, m indicates the molal concentration of the phosphate mixture, c_{NaCl} the concentration of the added sodium chloride, c the total equivalent concentration, $p_{H^\cdot}$ the measured hydrogen exponent, ρ_f the value of $\log f_2/f_1 + k$ calculated from equation (13) and ρ_e the value obtained from the curves in Fig. 2.

As our theory requires, the value of ρ_f is found to decrease steadily with increasing ionic concentration. Comparison with the values of ρ_e shows a fairly good agreement, the calculated values, however, always being somewhat smaller than those found. As emphasised in the introduction, the basis of our calculation is not sufficiently defined to permit us to expect a close agreement, no allowance having been made for the peculiarities of the various salt systems. There can be no doubt, however, that the figures in Table IV lend strong support to the general theory which underlies these calculations.

Very thorough investigations on acetate regulator mixtures have been published by Walpole (T., 1914, **105**, 2501, 2521). His work contains three series of measurements, namely (i) acetic acid–sodium acetate mixtures in which the total "acetate" was $0{\cdot}2N$, (ii) acetic acid–sodium acetate–sodium chloride solutions in which the total "acetate" was $0{\cdot}2N$ and the total sodium was $0{\cdot}2N$, and (iii) mixtures of acetic acid and sodium acetate in equal concentration ("*standard acetate*" *at various dilutions*). The three kinds of mixtures can be characterised by the following equations:

$$c_{C_2H_3O_2Na} + c_{C_2H_4O_2} = 0{\cdot}2 \quad . \quad . \quad . \quad \text{(i.)}$$
$$c_{C_2H_3O_2Na} + c_{C_2H_4O_2} = c_{C_2H_3O_2Na} + c_{NaCl} = 0{\cdot}2 \quad . \quad \text{(ii.)}$$
$$c_{C_2H_3O_2Na} = c_{C_2H_4O_2} \quad . \quad . \quad . \quad \text{(iii.)}$$

The results of the first series are given in Table V. The figures in the first column are the concentrations of the acetic acid; in the second and the third columns are given the observed *E.M.F.*'s and the hydrogen-ion concentrations calculated by Walpole. The figures in the last column are the values of $\rho = \log f_1/f_0 + k$ calculated by means of equation (10).

In equation (10) used for the calculation of ρ we have to introduce $c_0 = c_{C_2H_4O_2} - c_{H^\cdot}$ and $c_1 = c_{C_2H_3O_2Na} + c_{H^\cdot}$. Whilst $c_{H^\cdot}$ is negligible at concentrations of acetic acid lower than $0{\cdot}16$, we have to correct for it at higher concentrations. The figures under $c_{H^\cdot}$ are calculated by Walpole from the equation $\pi = 0{\cdot}3377 + 0{\cdot}0577 \log \dfrac{1}{c_{H^\cdot}}$ on the assumptions that the dissociation is 92 per cent. in $0{\cdot}1N$-hydrochloric acid and that the gas laws are valid in the case of the solutions concerned. Since both assumptions are erroneous, the values of $c_{H^\cdot}$ can be accurate only until $c_{C_2H_4O_2}$

TABLE V.

$c_{C_2H_4O_2}$.	π.	$c_{H^\cdot} \times 10^3$.	ρ.
0·0025	0·7138	—	0·473
0·005	0·6961	—	0·473
0·0075	0·6853	—	0·468
0·01	0·6778	—	0·468
0·02	0·6593	—	0·473
0·03	0·6478	—	0·474
0·04	0·6393	—	0·477
0·05	0·6316	—	0·469
0·06	0·6256	—	0·474
0·08	0·6148	—	0·479
0·1	0·6046	—	0·478
0·12	0·5947	—	0·483
0·14	0·5841	—	0·491
0·16	0·5712	0·09	0·500
0·18	0·5525	0·19	0·525
0·185	0·5450	0·26	0·528
0·190	0·5348	0·38	0·531
0·192	0·5290	0·48	0·522
0·194	0·5225	0·63	0·520
0·195	0·5193	0·71	0·531
0·196	0·5155	0·83	0·540
0·197	0·5105	1·01	0·537
0·198	0·5057	1·23	0·552
0·199	0·4995	1·57	0·545
0·2	0·4931	2·01	0·541

= 0·194. At higher concentrations the ρ-values, therefore, will be somewhat untrustworthy.

The results of the second series are given in Table VI.

TABLE VI.

$c_{C_2H_4O_2}$.	π.	$c_{H^\cdot} \times 10^3$.	ρ.
0·004	0·7015	—	0·468
0·0105	0·6762	—	0·462
0·04	0·6375	—	0·447
0·06	0·6235	—	0·438
0·08	0·6126	—	0·441
0·1	0·6019	—	0·432
0·12	0·5908	—	0·405
0·14	0·5793	—	0·408
0·16	0·5654	0·142	0·399
0·17	0·5564	0·162	0·394
0·18	0·5461	0·244	0·414
0·185	0·5389	0·326	0·420
0·189	0·5297	0·471	0·395
0·19	0·5274	0·515	0·396
0·194	0·5159	0·817	0·393
0·195	0·5129	0·920	0·405
0·199	0·4949	1·89	0·376
0·2	0·4902	2·77	0·436

The notation and the calculation are here the same as in the foregoing case.

Finally in Table VII the third series of measurements is pre-

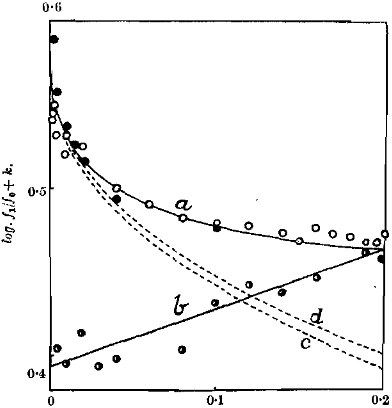
sented; c here indicates the equal concentrations of acetic acid and sodium acetate.

TABLE VII.

c.	π.	ρ.
0·2	0·60345	0·458
0·1	0·60445	0·476
0·04	0·60575	0·496
0·02	0·60678	0·517
0·016	0·60735	0·526
0·01	0·60798	0·536
0·005	0·60923	0·558
0·002	0·61100	0·589
0·001	0·61223	0·611

The results of the three series are shown diagrammatically in Fig. 4, which can most conveniently be made a basis for discussion. The values of ρ, differing from the values of $\log f_1/f_0$ only by a constant, are here plotted as ordinates against the concentrations of sodium acetate as abscissæ. The data belonging to series (i), (ii) and (iii) are indicated by o, ◑ and ● respectively.

FIG. 4.



Concentration of sodium acetate.

First of all, through the mutual position of the points in the diagram, we obtain information about the experimental error.

This amounts in many cases to 0·05 or more, expressed in p_H-values. Nevertheless, there can be no doubt how to draw the most fitting curve through the experimental points. It is evident that the measurements in series (i) and (iii) are represented by a strongly bent curve, *a*, identical for both series. The measurements of series (ii), on the other hand, lie probably on a straight line *b*.

This, however, is just what we have to expect from the point of view of our theory. In (i) and (iii) no salt is present other than *sodium acetate*. Independently of the amounts of acetic acid, which differ largely in the two series, we must find concordant values of f_1/f_0 at the same concentration of sodium acetate. The shape of the curve, furthermore, agrees well with the theoretical one given in Fig. 2. In the second series, on the other hand, the salt present in the solution changes gradually from 0·2 molal sodium chloride to 0·2 molal sodium acetate, the total salt concentration being constant. Here we have to expect a salt effect changing proportionately with the change in composition, that is, a rectilinear change in f_1/f_0, as exhibited by the experiments.

The course of the line *b*, inclining strongly from sodium acetate to sodium chloride solution, gives evidence of the fact that the salt effect is markedly a function of the nature of the salt in question. On the assumption that the effect of the two salts is an additive one, the curve *c* in the figure is calculated as expressing the interdependence of log f_1/f_0 and the concentration in a solution containing no other salt than sodium chloride. The theoretical curve based upon the solubility measurements referred to in the introduction is inserted in Fig. 4 as *d*. This curve evidently agrees rather closely with the sodium chloride curve, *c*, in accordance with the fact that acetates deviate more than chlorides from the average salt effect as given in the theoretical curves in Fig. 2.

4. *The Indicator Equilibrium.*

Another field in which our theory can be applied advantageously is the much discussed problem of the influence of salts on the colours of indicators. (For the literature, see Bjerrum: "Die Theorie der alkalimetrischen und azidimetrischen Titrierungen, Sammlung Ahrens," 1914.) Since the functions of indicators, according to the view introduced by Ostwald, are due to their properties as weak acids and weak bases, this problem is a special case of the one treated in the foregoing.

The particular advantage of using solutions of indicators consists in the possibility of deducing from the colour the ratio in which the undissociated and the dissociated portions are present in the

solutions. Assume the case of an acid indicator dissociating according to the scheme :

$$SH \rightleftarrows S' + H^{\cdot}$$

then equation (10) will apply thermodynamically to this equilibrium. When the solutions considered show the same colour, c_1/c_0 in this equation will be a constant and therefore :

$$\log \frac{f_1}{f_0} = k + p_{H^{\cdot}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

As a consequence of this equation a given activity of the hydrogen ion will produce the same colour only in solutions having the same value of f_1/f_0. The colorimetric method for the determination of hydrogen-ion activities, based upon the principle of comparing the colour of a series of regulator mixtures with the colour of the solution the hydrogen-ion activity of which is to be determined, will therefore to a certain degree be untrustworthy if the concentration of the solution differs from that of the regulator mixtures. Equation (14) teaches that in the case of an acid indicator the addition of salts, that is, decreasing values of f_1/f_0, implies decreasing values of $p_{H^{\cdot}}$. The *more concentrated solution is more acid than the less concentrated which gives the same colour.* The colorimetric *method consequently leads us to accept too small a hydrogen-ion activity in the concentrated solution.*

In the case of a basic indicator we can write, instead of (14),

$$\log \frac{f_1}{f_0} = k - p_{H^{\cdot}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

and therefore follow an effect in the opposite direction. The colorimetric method leads us to accept too high a hydrogen-ion activity in the more concentrated solution.

A verification of these conclusions is furnished by the investigations of Sörensen (*loc. cit.*) and his co-workers, who have done important work for the elaboration of the colorimetric method. The test is made a quantitative one by introducing in equations (14) and (15) the values of f_1/f_0 and f_2/f_1 calculated on the principles given in the introduction.

Sörensen's data are tabulated in Table VIII. The first column gives the indicator used. The column headed $(p_{H^{\cdot}})_c$ contains the values of $p_{H^{\cdot}}$ found colorimetrically by comparison with the pure regulator without added salt; $(p_{H^{\cdot}})_e$ is the electrometric or true value of $p_{H^{\cdot}}$ in the solution. The "salt error" is defined by :

$$\Delta = (p_{H^{\cdot}})_e - (p_{H^{\cdot}})_c$$

Δ_f and Δ_c indicating the observed and the calculated values of the salt error respectively.

TABLE VIII.

Indicator.	$(p_{H^{\cdot}})_c$.	Δ_f.	Δ_c.
(1) Solution: Phosphate (0·07N) + NaCl (0·5N); $(p_{H^{\cdot}})_s$ = 5·65.			
p-Nitrophenol	5·81	+ 0·16	+ 0·15
p-Sulphobenzeneazo-α-naphthylamine	5·55	− 0·10	− 0·15
Alizarinsulphonic acid	5·91	+ 0·26	+ 0·23
(2) Solution: Phosphate (0·11N) + NaCl (0·5N); $(p_{H^{\cdot}})_s$ = 6·66.			
p-Nitrophenol	6·80	+ 0·14	+ 0·14
Neutral-red	6·57	− 0·09	− 0·14
Rosolic acid	6·72	+ 0·06	+ 0·14
(3) Solution: Borate (0·08N) + NaCl (0·5N); $(p_{H^{\cdot}})_s$ = 8·02.			
p-Sulphobenzeneazo-α-naphthol	8·14	+ 0·12	+ 0·15
Phenolphthalein	8·14	+ 0·12	+ 0·15

It is seen that the effect of the salt on the various indicators in nearly all cases agrees well with the calculated effect. Only in the case of rosolic acid is the agreement less satisfactory.

In Table IX are given some other data from some measurements of Sörensen and Palitzsch (*Medd. Carlsberg Lab.*, 1913, **10**, 228).

TABLE IX.

c.	Δ_f. (I.)	Δ_c. (I.)	Δ_f. (II.)	Δ_c. (II.)
0·01	− 0·09	− 0·06	− 0·14	− 0·11
0·02	− 0·05	− 0·04	− 0·12	− 0·09
0·05	− 0·02	0	− 0·07	− 0·05
0·1	+ 0·05	+ 0·03	− 0·02	− 0·02
0·2	+ 0·11	+ 0·07	+ 0·05	+ 0·02
0·5	+ 0·20	+ 0·15	+ 0·14	+ 0·10

c is the concentration of the salt solution and Δ_f and Δ_c have the same meaning as above. Series I refers to measurements in which phenolphthalein and naphtholphthalein were used as indicators in solutions of a borate mixture of concentration 0·05. In series II phenolphthalein and phosphate mixtures were employed. A comparison of Δ_f and Δ_c shows the anticipated salt effect. That the calculated values are somewhat smaller than those found is perhaps due to the assumption, made in calculations according to equation (14), that the indicators are monobasic acids. Assuming the indicators to dissociate as dibasic acids—and for this assumption some evidence has been brought forward (Wegscheider, *Zeitsch. Elektrochem.*, 1908, **14**, 510)—we must introduce f_2/f_1 instead of f_1/f_0, and then obtain small deviations in the opposite direction.

The effect of salts on indicators has been examined from the point of view that the hydrogen-ion activity is the deciding factor in the indicator equilibrium. The displacement of the equilibrium in an indicator-regulator mixture, however, can be considered from another point of view, namely, that the equilibrium can be represented with no hydrogen ions entering in the equilibrium scheme.

Denoting the neutral molecules of an acid and a basic regulator by AH and B respectively, and the neutral molecules of an acid and a basic indicator by SH and M, all possible equilibria and the effect of the addition of salts on any of these can be given by the following scheme :

	Indicator.	*Regulator.*	*Equilibrium.*	*Effect.*
(I)	acid	acid	$SH + A' \rightleftarrows S' + AH$	none
(II)	acid	basic	$SH + B \rightleftarrows S' + BH^{\cdot}$	more basic
(III)	basic	acid	$MH^{\cdot} + A' \rightleftarrows M + AH$	more acid
(IV)	basic	basic	$MH^{\cdot} + B \rightleftarrows M + BH^{\cdot}$	none

The requirements of this scheme seem actually to be fulfilled in most cases of observations with indicators of known chemical nature, especially when it is noted that the requirement of " none " effect cannot be at all a rigid one, because even very small deviations from equal salt effect on ions of the same type will be able to produce a change in colour of the indicator.

As an example we may quote the very accurate investigation carried ont in this field by Rosenstein (*J. Amer. Chem. Soc.*, 1912, **34**, 1125) who evaluated directly the colour change of phenolphthalein to determine the degree of dissociation of this indicator in an ammonia–ammoninm chloride regulator in which $c_{NH_4^{\cdot}}/c_{NH_3}$ was kept constant. In Table X the ratios $\frac{\alpha}{1-\alpha}$ are given together with the corresponding total salt concentrations c_t, the values of f_1/f_0 taken from the diagram (Fig. 2) and finally the value of $r = \frac{\alpha}{1-\alpha} \Big/ \left(\frac{f_0}{f_1}\right)^2$.

TABLE X.

c_t.	$\frac{\alpha}{1-\alpha}$	f_1/f_0.	r.
0·10	0·246	0·69	0·116
0·13	0·261	0·67	0·118
0·20	0·310	0·63	0·122
0·60	0·469	0·50	0·117

Since we have here a basic regulator and an acid indicator the system will be represented by the equilibrium (II) in the above scheme. Increasing salt concentration, therefore, must render the solution more basic, as is really shown by the figures in the second column. For the equilibrium (II) the thermodynamic mass-action law requires

$$\left(\frac{\xi_1}{\xi_0}\right)^2 = \frac{c_{NH_4^{\cdot}}}{c_{NH_3}} \cdot \frac{\alpha}{1-\alpha}\left(\frac{f_1}{f_0}\right)^2 = \text{constant}$$

or as $\frac{c_{NH_4^{\cdot}}}{c_{NH_3}}$ was unchanged

$$\frac{\alpha}{1-\alpha} \cdot \left(\frac{f_1}{f_0}\right)^2 = \text{constant.}$$

The constancy of this term is exhibited by the values of r given in the last column.

Some other series of the measurements of Rosenstein harmonise more fully with the assumption of the dissociation of phenolphthalein as a dibasic acid.

As a chief result of our considerations of the effects of salts on the indicator equilibrium we may record the complete agreement of the theory in regard to the sign, and the partial agreement in regard to the magnitude, of the effect with the evidence furnished by various materials and in various fields of investigation. For reasons stated in the introduction, however, all our calculations are to a certain degree approximate, and in the case of indicators a special uncertainty attends the numerical results on account of the chemical nature of such substances not being fully elucidated; for example, methyl-orange, which is usually regarded as a basic indicator on account of its character as amine. Simultaneously acting as a strong acid, the anion of this will be the form in which the indicator will be present in alkaline solution, and the equilibrium scheme of the dissociation therefore will be represented by

$$(CH_3)_2N{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3^- + H^+ \rightleftarrows {}^{(CH_3)_2}_{H}\!\!>\!\overline{N{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3}$$

fully corresponding with the dissociation of an acid indicator if we are allowed to regard the right-hand molecule as electrically a neutral one. This, however, is doubtful, because one hydrogen ion has been removed from one end of the molecule and added to the other and the electric charges produced do not necessarily neutralise one another; therefore, it can be foretold that the behaviour of such a substance will be uncertain.

Similar uncertainties, and also others due to the possibly colloidal nature of the indicator, are encountered in many cases.

Summary.

From the point of view of the theory of complete dissociation of strong electrolytes, the interpretation of the solubility phenomena exhibited by slightly soluble salts leads us to surmise an increase in the dissociation of weak electrolytes on the addition of salts to their solutions. Evidence corroborative of this conclusion has been advanced from various fields of investigation, and an explanation of the salt effect on regulator mixtures and indicator equilibria has been given from the same point of view.

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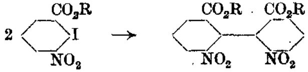
[*Received, December 28th, 1920.*]

LXIV.—*A Second Form of 6 : 6′-Dinitrodiphenic Acid, and its Conversion into New Cyclic Systems.*

By JAMES KENNER and WILFRID VICTOR STUBBINGS.

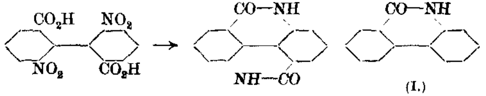
IN connexion with another investigation, it became desirable to prepare 6 : 6′-dinitrodiphenic acid. This compound was first obtained by Schulze (*Annalen*, 1880, **203**, 95) as one of the products of nitration of diphenic acid, and also of oxidation of the mixture of dinitro-derivatives obtained from phenanthraquinone. Its probable constitution, although recognised by Schad (*Ber.*, 1893, **26**, 219), was first demonstrated by Schmidt (*Ber.*, 1903, **36**, 3745), who prepared 2 : 2′-dinitrodiphenyl from it by distillation of the barium salt, and obtained carbazole in a similar manner from the corresponding diamino-acid, which Schad (*loc. cit.*) had prepared and characterised. The synthesis of the acid had, however, not been carried out, and we therefore proposed to complete the evidence just summarised by preparing our material synthetically.

2-Chloro-3-nitrobenzoic acid was obtained by oxidation of 2-chloro-3-nitrotoluene with dilute nitric acid, whilst the preparation of the corresponding iodo-acid has recently been described by us (T., 1920, **117**, 776). The *esters* of either of these acids, but preferably of the latter, reacted easily with copper powder, and furnished the esters of the desired acid :



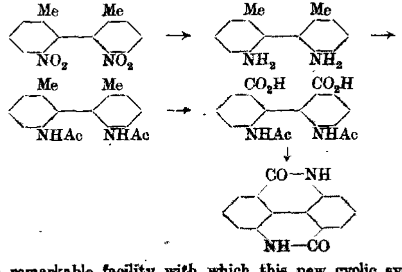
The melting point of the dimethyl ester prepared in this manner was almost the same as that given by Schulze (*loc. cit.*), but, to our surprise, the acid obtained from it by hydrolysis melted at 263°, without decomposition, as against 297° (Schulze) or 303° (Schmidt) with decomposition. Unfortunately, Schulze's acid has not been characterised by means of other derivatives; we hope to rectify this omission. Meanwhile, the two acids are clearly differentiated by their behaviour on reduction. Whilst, as already indicated, a diamino-acid is obtained from Schulze's acid in the ordinary manner, the new γ-acid* furnishes an internal anhydride :

* Schulze termed his acid β-dinitrodiphenic acid to distinguish it from the α(3 : 3′)-acid produced simultaneously. Pending, therefore, a decision as to the configurations of the two 6 : 6′-dinitro-acids, it seems less likely to lead to confusion if the new acid is distinguished as the γ-acid.



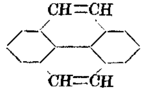
(I.)

The constitution of this compound is shown, not merely by its composition and mode of formation, but also by its close analogy to phenanthridone (I). Thus, it may be sublimed, and is very sparingly soluble in all the usual solvents. It readily dissolves, however, in concentrated sulphuric acid, and the solution exhibits a beautiful, blue fluorescence. It is insoluble in aqueous solutions of alkalis, but is dissolved by concentrated, alcoholic potassium hydroxide solution, being, however, reprecipitated on dilution with water. So great is the tendency to form the new cyclic system, that this forms the chief product even when ethyl γ-dinitrodiphenate is carefully reduced. Evidence of the production of the true ethyl γ-diaminodiphenate was obtained, but internal condensation took place when the attempt was made to isolate this compound. Subsequently, the dilactam was synthesised by another method, which is more convenient for its preparation in a state of purity. 6 : 6′-Dinitroditolyl, prepared by the action of copper powder on 2-chloro-3-nitro-, or, preferably, 2-iodo-3-nitrotoluene, was converted into the corresponding *diamino*-compound. By oxidation of 6 : 6′-*diacetylamino*-2 : 2′-*ditolyl* with potassium permanganate in neutral solution, γ-6 : 6′-*diacetylaminodiphenic acid* was easily obtained. This substance at once yielded the dilactam when treated with the usual hydrolysing agents, and also even when heated with acetic anhydride :

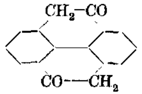


The remarkable facility with which this new cyclic system is produced is in contrast with the difficulty of synthesising the un-

saturated ring systems of pyrene (III) (Mayer, *Ber.*, 1911, **44**, 2298). This was only achieved by first preparing diketotetrahydropyrene (IV), which was obtained fairly readily from diphenyl-2 : 2′-diacetyl

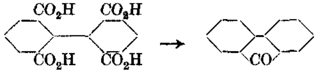


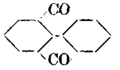
(III.)



(IV.)

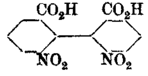
chloride (Weitzenböck, *Monatsh.*, 1913, **34**, 199). In other words, *saturated systems of this type are produced much more readily* than the corresponding unsaturated ones. Apparently, also, two six-membered rings are obtained more easily than two five-membered rings, for R. Meyer, W. Meyer, and K. Falger have recently shown that fluorenone is produced in place of the compound (V) when diphenyl-2 : 6 : 2′ : 6′-tetracarboxylic acid is distilled (*Ber.*, 1920, **53**, [*B*], 2034) :

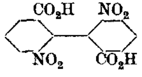




(V.)

It seems clear therefore that 6 : 6′-dinitrodiphenic acid, like 3 : 3′-dinitrobenzidine (Cain and others, T., 1912, **101**, 2298; 1913, **103**, 2074; 1914, **105**, 1437, 1442) exists in two forms, which can scarcely be other than stereoisomeric, and may be represented by the formulæ :

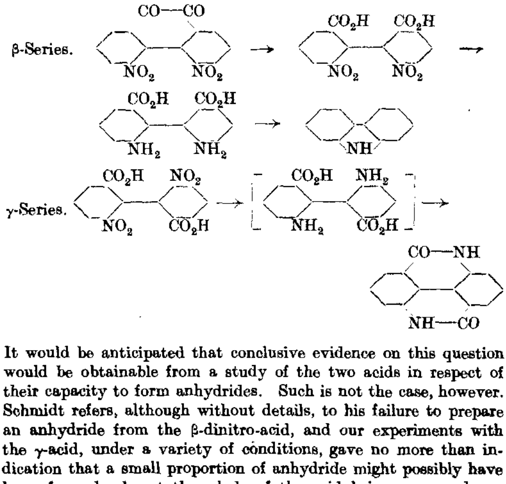




Cain and his collaborators, from other considerations than that of the isomerism of their compounds, were led to adopt the Kaufler formulæ for them. We prefer to leave the question of the relative merits of these and the ordinary formulæ open for the present, although it may be said that our experiments originated with an attempt to obtain further evidence on this point.

The relative configurations of the various compounds now under discussion are perhaps best deduced in the following manner. The diaminodiphenic acid initially obtained by the reduction of γ-dinitrodiphenic acid evidently differs from that prepared from the β-acid, which resisted a number of attempts, recorded by Schad

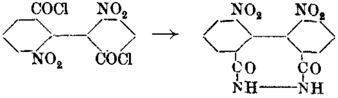
(*loc. cit.*), to obtain an internal condensation product from it. These acids have therefore a definite configuration, the unstable acid being a *trans*-, and Schad's acid a *cis*-compound. Further, unless the improbable assumption is made that in each case reduction is accompanied by inversion, the dinitro-acids have similar configurations. This view, which seems to have been entertained by Schmidt in regard to the β-acid, accords with its formation from 4 : 5-dinitrophenanthraquinone, and with the preparation of carbazole from the β-diamino-acid, although this is a high-temperature reaction and hence perhaps less valuable as evidence. The several relationships are therefore to be represented as follows :



It would be anticipated that conclusive evidence on this question would be obtainable from a study of the two acids in respect of their capacity to form anhydrides. Such is not the case, however. Schmidt refers, although without details, to his failure to prepare an anhydride from the β-dinitro-acid, and our experiments with the γ-acid, under a variety of conditions, gave no more than indication that a small proportion of anhydride might possibly have been formed, almost the whole of the acid being recovered unchanged in every case. Unexpected as these results may appear, they are in agreement with the behaviour of diphenyl-2 : 6 : 2′ : 6′-tetracarboxylic acid, which, as we hope to show in a subsequent communication, also does not give an anhydride.

The stability of configuration of the two dinitrodiphenic acids is apparently not maintained when the chloride of the new acid is treated with hydrazine. Reaction readily takes place, giving

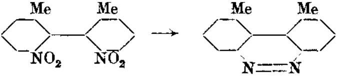
rise to the " hydrazide " (VI), which, in accordance with the formula assigned to it, is soluble in alkali and gives a well-defined *diacetyl* derivative :



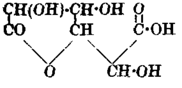
(VI.)

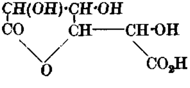
In view of this result, it appeared possible that by alkaline hydrolysis of the γ-acid chloride the β-acid might be obtained, but experiment showed that the original acid is recovered. Apparently, then, change of configuration occurs, not in the formation of the chloride, but when the chloride is treated with hydrazine.

Further, since 1 : 10-*dimethyl*-5 : 6-*naphthaisodiazine* is easily obtained from 6 : 6′-dinitro-2 : 2′-ditolyl by reduction with sodium amalgam :



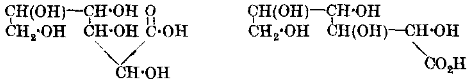
it is clear that either this compound has not a definite configuration, or inversion takes place at some stage during its conversion into γ-6 : 6′-diacetylaminodiphenic acid or during the reduction itself. The last is perhaps the simplest assumption, since the above change of configuration seems to be due to the influence of a base. Instances of this kind are familiar in the sugar group, and the following considerations suggest another which seems to have been overlooked. Of the saccharic acids, mannosaccharic acid alone forms a dilactone (E. Fischer, *Ber.*, 1894, **27**, 3227). The monolactone of saccharic acid is therefore presumably to be represented by one of the two formulæ :





The first assumes a definite configuration, unfavourable to lactonisation, of the groups attached to the carbon atom of the carboxyl group, in accordance with the suggestion of Irvine and Steele (T., 1915, **107**, 1221) that the groups attached to the terminal

carbon atoms of the mannitol molecule have a definite configuration. The second formula is perhaps less probable in view of the relationship between glucose and mannose, and the formation of a dilactone from mannosaccharic acid. Corresponding with the alternatives shown, the formula for gulonic acid would he one of the following:



Obviously, however, neither of these explains the formation of gulolactone. It seems, therefore, difficult to escape from the conclusion that inversion has occurred at some stage, and presumably under the influence of alkali.

EXPERIMENTAL.

2-*Chloro*-3-*nitrobenzoic Acid*.*

2-Chloro-3-nitrotoluene † is boiled under reflux with three parts by weight of nitric acid (D 1·37) for several days until homogeneity is attained, and no oil separates on cooling, nitric acid being added, if necessary, from time to time to maintain the bulk of the liquid. The acid, which crystallises on cooling, is purified by crystallisation from xylene. The product, m. p. 181° (Hollemann and de Bruyn, *Rec. trav. Chim.*, 1901, **20**, 206, give 185°), is sufficiently pure for further use. A very impure product is obtained by preparing the acid from 3-nitroanthranilic acid.

The *methyl* ester separates from light petroleum in needles, m. p. 70° (Found: N = 6·65. $C_8H_6O_4NCl$ requires N = 6·49 per cent.).

The *ethyl* ester boils at 314° with some decomposition (Found: N = 6·22. $C_9H_8O_4NCl$ requires N = 6·10 per cent.).

γ-6 : 6′-*Dinitrodiphenic Acid*.

Methyl 2-chloro-3-nitrobenzoate (10 grams) was treated gradually at 210° with copper powder (10 grams), and the mixture then

* Certain of the compounds now described were first prepared by Mr. C. W. James, M.Sc., in collaboration with one of us. These are distinguished by an asterisk.

† The 3-nitro-*o*-toluidine from which this substance was prepared was obtained more consistently, more rapidly, and, probably, more cheaply by Hadfield and Kenner's method (P., 1914, **28**, 253) than by either of those described by Gabriel and Thieme (*Ber.*, 1919, **52**, [*B*], 1079), and by Meisenheimer and Hesse (*ibid.*, 1171).

heated at 225—235° for one hour. By extracting the cold mass with benzene, and crystallisation from this solvent, *methyl γ-6 : 6′-dinitrodiphenate* (5 grams) was obtained in pale yellow, hexagonal plates, m. p. 132—133° (Found: N = 8·00. $C_{16}H_{12}O_8N_2$ requires N = 7·78 per cent.).

Ethyl γ-6 : 6′-dinitrodiphenate, $C_{18}H_{16}O_8N_2$, was prepared in a similar manner from *ethyl 2-iodo-3-nitrobenzoate* (large, tabular crystals, m. p. 54°. Found: N = 4·43. $C_9H_8O_4NI$ requires N = 4·36 per cent.), reaction occurring at 155°. After purification, it formed large, yellow crystals, m. p. 140—142° (Found: N = 7·37. $C_{18}H_{16}O_8N_2$ requires N = 7·12 per cent.).

γ-6 : 6′-*Dinitrodiphenic acid*, $C_{14}H_8O_8N_2$, was obtained by boiling the esters (1 gram) with sulphuric acid (20 c.c.) and water (17 c.c.) until the oil had disappeared. The acid, which separated on cooling, was purified by crystallisation from either glacial acetic acid or benzene, and thus obtained in thin plates, m. p. 258—259°. A sample of the acid, however, which had been regenerated from its chloride by means of dilute sodium hydroxide solution, melted sharply at 263° (Found: N = 8·43; equivalent = 166. $C_{14}H_8O_8N_2$ requires N = 8·43 per cent.; equivalent = 166). The *stannous, silver, lead, ferric*, and *copper* salts are sparingly soluble in water, the lead salt alone being appreciably more soluble in hot water and separating in an indistinctly crystalline condition on cooling. The *mercuric, cobalt, calcium, magnesium*, and *barium* salts are soluble in water.

A number of attempts were made to convert the acid into an anhydride by heating it with acetic anhydride either at the boiling point, or under pressure at 140°, alone, or in presence of a small amount of phosphoryl chloride. In all cases, the main portion of the acid was recovered unchanged. Elementary analysis of material, of which the equivalent was sensibly diminished, indicated that this was due rather to traces of acetic anhydride than to the desired anhydride. Attempts to prepare a monomethyl ester from any anhydride present by means of sodium methoxide were also fruitless.

The *chloride* forms prisms, m. p. 157° (Found: N = 7·75. $C_{14}H_6O_6N_2Cl_2$ requires N = 7·59 per cent.).

The *amide* separates from alcohol in crystals, m. p. 276°, with decomposition (Found: N = 17·14. $C_{14}H_{10}O_6N_4$ requires N = 16·97 per cent.).

The *dianilide* forms flat, diamond-shaped crystals, m. p. 232—234°, with decomposition (Found: N = 11·44. $C_{26}H_{18}O_6N_4$ requires N = 11·62 per cent.).

The "*hydrazide*" (formula VI, p. 597) was prepared by shaking

a solution of the dichloride in benzene with a solution of hydrazine hydrate, prepared from hydrazine sulphate (6 grams). The precipitate was purified by boiling first with water, and then with alcohol. Thus obtained, it blackened without melting above 290°, but was evidently not quite pure (Found: N = 16·35. $C_{14}H_8O_6N_4$ requires N = 17·08 per cent.). It was soluble in cold sodium hydroxide solution, giving a yellow solution, but not in dilute ammonia solution.

The *diacetyl* derivative of the "*hydrazide*," $C_{18}H_{12}O_8N_4$, was prepared by heating a mixture of the hydrazide (1 gram) with *acetic anhydride (4 c.c.) and anhydrous sodium acetate (2 grams)* for fourteen hours at 150°. By crystallisation from benzene, small prisms, m. p. 214—215°, were obtained (Found: C = 52·16; H = 2·98; N = 13·87. $C_{18}H_{12}O_8N_4$ requires C = 52·43; H = 2·91; N = 13·59 per cent.).

6 : 6′-*Diamino*-2 : 2′-*ditolyl*.

This compound was prepared by the reduction of 6 : 6′-dinitroditolyl, m. p. 111—112° (Ullmann and Frentzel, *Ber.*, 1905, **38**, 725, give 110°), *at the ordinary temperature in glacial acetic acid* solution by means of stannous chloride and hydrochloric acid. It separates from alcohol in clusters of slender needles, m. p. 136° (Found: N = 13·22. $C_{14}H_{16}N_2$ requires N = 13·20 per cent.).

The *diacetyl* derivative, was produced immediately on the addition *of acetic anhydride to the base, and in a condition sufficiently pure* for the subsequent oxidation. It separated from aqueous alcohol in clusters of transparent needles, m. p. 205° (Found: N = 9·65. $C_{18}H_{20}O_2N_2$ requires N = 9·46 per cent.).

γ-6 : 6′-*Diacetylaminodiphenic Acid*.

6 : 6′-Diacetylamino-2 : 2′-ditolyl (7·2 grams) was boiled with a solution of potassium permanganate (20·8 grams), and crystallised magnesium sulphate (15·2 grams) in water (1040 c.c.) until the solution was decolorised. *The filtered solution was concentrated* to 250 c.c., cooled, and acidified with sulphuric acid. The product showed a marked tendency to form supersaturated solutions, and usually did not separate until the measures usual in such cases had been taken, when it was obtained in large prismatic crystals. At higher temperatures needles were obtained, but these gave place to prisms when a sample of these was added at the ordinary temperature. The acid did not melt below 300°. For analysis it was crystallised from methyl alcohol (Found: N = 7·83;

equivalent = 180. $C_{18}H_{16}O_8N_2$ requires N = 7·86 per cent.; equivalent = 178).

The Dilactam of γ-6 : 6′-Diaminodiphenic Acid.

A. *From γ-6 : 6′-dinitrodiphenic acid.*—A solution of the acid (0·9 gram) in glacial acetic acid (25 c.c.) was treated with concentrated hydrochloric acid (18 c.c.) and stannous chloride (6·3 grams), and the mixture heated until solution was complete. It was not found possible to free the bulky white precipitate from tin by the usual methods. This was achieved, however, by sublimation, although the process was very tedious and wasteful. (A more convenient procedure, subsequently discovered, is described below.) In this way pale yellow needles were obtained, which were insoluble in all the usual solvents (Found: N = 11·99, 12·30. $C_{14}H_8O_2N_2$ requires N = 11·86 per cent.).

B. *From ethyl γ-6 : 6′-dinitrodiphenate.*—The reduction of the ester was carried out in a similar manner to that of the acid, with the exception that the temperature was kept below 40°. A separation occurred in this case also, but a small proportion (*ca.* 20 per cent.) of the material was obtained as a basic oily substance in the usual manner. Even at the ordinary temperature, however, this slowly changed into a sparingly soluble yellow product, which seemed to be a *carbethoxyaminophenanthridone* (Found: C = 62·16; H = 5·04; N = 10·46. $C_{16}H_{14}O_3N_2$ requires C = 68·10; H = 4·96; N = 9·93 per cent.).

The material from the reduction, which was insoluble in alkali or in ether, easily dissolved in warm concentrated sulphuric acid. On gradual addition of water, greenish-yellow prisms separated, which were purified by recrystallisation in a similar manner (Found: N = 11·70, 11·41 per cent.).

C. *From diacetyldiaminodiphenic acid.*—(1) The acid (5 grams) was boiled with acetic anhydride (50 grams). A finely divided solid was almost at once produced, but the operation was continued for ten hours. The material obtained was insoluble in all the usual solvents, and was purified by boiling it with benzene (Found: N = 11·97 per cent.).

(2) The acid (1 gram) was boiled with 70 per cent. sulphuric acid (6 c.c.) for twenty-five minutes. Separation of a pale yellow solid commenced almost immediately, and a further quantity was finally obtained by dilution (Found: C = 67·90, 67·90; H = 3·72, 3·72; N = 11·91. $C_{14}H_8O_2N_2$ requires C = 71·19; H = 3·39; N = 11·86 per cent.).

The material from each of these experiments did not melt below

300°, and could be sublimed. It was insoluble in all the usual solvents, but easily soluble in concentrated sulphuric acid, giving a solution with a beautiful blue fluorescence. It also dissolved in concentrated alcoholic potassium hydroxide solution, but was reprecipitated on dilution with water. In all these respects it corresponds exactly with phenanthridone. It will be noted that the values for carbon are in each case very low, but they are much too high for alternatively possible formulæ, for example, a compound with only one lactam ring. Even these results, however, were only obtained when the material was mixed with lead chromate and potassium dichromate in a combustion tube packed with lead chromate. Under ordinary conditions the result was 15—20 per cent. too low. The satisfactory agreement of the values for hydrogen and nitrogen leaves little room for doubt as to the composition of the material.

1 : 10-*Dimethyl*-5 : 6-*naphthaisodiazine*.

A *solution of* 6 : 6′-dinitroditolyl (5·6 grams) in methyl alcohol (200 c.c.) was treated in the course of forty-five minutes with 3 per cent. sodium amalgam (250 grams), with cooling. The alcoholic solution, after concentration, was diluted with water. The precipitated material was purified by crystallisation from dilute alcohol, and obtained in pale yellow, transparent prisms, m. p. 96—97° (*Found*: N = 13·57. $C_{14}H_{12}N_2$ *requires* N = 13·46 per cent.).

The authors wish to express their thanks to The British Dyestuffs Corporation for supplies of o-toluidine, and to Messrs. Whiffen and Son for the sodium iodide, used in these experiments. One of them also wishes to thank the Corporation for the opportunity of collaborating in this work.

THE UNIVERSITY,
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[*Received, February 22nd*, 1921.]

LXV.—*Arylsulphonylnaphthylenediamines and their Sulphonic Acids.*

By GILBERT T. MORGAN and WILLIAM ROBINSON GRIST.

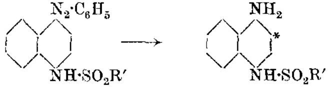
THE reactions described below constitute a simple and general method of preparing the arylsulphonyl derivatives of 1 : 4-naphthylenediamine and their sulphonic acids. Hitherto the only known

member of this series, benzenesulphonyl-1 : 4-naphthylenediamine, has been obtained by a roundabout process from α-naphthylamine through 4-nitro-α-naphthylamine by converting the latter substance into its benzenesulphonyl derivative and by reducing the latter (Morgan and Micklethwait, T., 1905, **87**, 1308).

O. N. Witt and Schmitt (*Ber.*, 1894, **27**, 2370) showed that toluene-*p*-sulphonyl-α-naphthylamine coupled with benzenediazonium chloride, giving a para-azo-derivative (I) from which by reduction they obtained 1 : 4-naphthylenediamine.

We have found, however, that the reduction can be effected smoothly and completely without the removal by hydrolysis of the arylsulphonyl group. Accordingly, while one reduction product is aniline, which can be recovered quantitatively, the other is toluene-*p*-sulphonyl-1 : 4-naphthylenediamine (II).

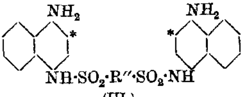
This reaction has been generalised by examining a large number of cases, and in every instance the arylsulphonyl-1 : 4-naphthylenediamine (II) has been obtained readily and in satisfactory yield (Eng. Pat., *application* 19392/19. Fr. Pat. 132339). The com-



(I.) (II.)

pounds represented by the general formula II are useful synthetic agents having a high degree of stability when compared with the very oxidisable *1 : 4-naphthylenediamine. They contain, in the* position marked by an asterisk, a reactive hydrogen atom which undergoes replacement in the production of ortho-azo-dyes, thiazole derivatives, and other substitution products which are under investigation.

The symbol R′ represents a univalent aromatic radicle, such as phenyl, tolyl, α- or β-naphthyl. This general reaction has also been extended to the production of more complex arylenedisulphonylbis-1 : 4-naphthylenediamines having the group formula (III).

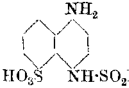


(III.)

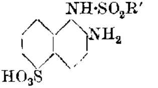
where R″ is a bivalent radicle such as 1 : 3-phenylene or a naphthylene group.

The arylsulphonyl-α-naphthylamines and arylenedisulphonylbis-α-naphthylamines produced by condensing α-naphthylamine respectively with arylsulphonyl and arylenedisulphonyl chlorides all couple readily with diazonium salts such as benzenediazonium chloride to yield the aryl-4-azo-derivatives (I).

By modifying the experimental conditions the α-naphthylamine-sulphonic acids can be condensed with arylsulphonyl chlorides to furnish arylsulphonyl-α-naphthylaminesulphonic acids. When the sulphonic group is in position 6, 7, or 8, the arylsulphonyl derivatives give 4-azo-compounds reducible to 1 : 4-naphthylenediamine derivatives, those from α-naphthylamine-8-sulphonic acid being represented by the formula IV. With the sulphonic group in position 4 or 5, one obtains 2-azo-compounds which on reduction yield derivatives of 1 : 2-naphthylenediamine, those from α-naphthylamine-5-sulphonic acid being indicated by formula V.



(IV.)



(V.)

Of the two groups of substituted diamines, the para-series (IV) give yellow diazo-derivatives coupling to form azo-compounds with phenols and the more reactive aromatic amines, whereas the ortho-series (V) furnishes non-coupling ortho-diazoimides.

EXPERIMENTAL.

I. *Arylsulphonyl*-1 : 4-*naphthylenediamines* (*General Formula II*).

Benzenesulphonyl-1 : 4-naphthylenediamine, the simplest member of this series (Morgan and Micklethwait, *loc. cit.*), more conveniently prepared from benzene-4-azobenzenesulphonyl-α-naphthylamine by reduction with zinc dust and dilute sodium hydroxide solution as detailed below, was obtained in acicular crystals melting at 188° (Found : N = 9·52. Calc., N = 9·39 per cent.).

(i) *Toluene*-p-*sulphonyl*-1 : 4-*naphthylenediamine*, $C_7H_7{\cdot}SO_2{\cdot}NH{\cdot}C_{10}H_6{\cdot}NH_2$.

The starting-point in this preparation was toluene-*p*-sulphonyl-α-naphthylamine, made by triturating 2 parts of α-naphthylamine with 3 parts of *p*-toluenesulphonyl chloride in the presence of 2 parts of fused sodium acetate, the final product being obtained in theor-

etical yield after the mixture had been washed successively with warm $2N$-sodium carbonate solution and hot water.

Benzene-4-azotoluene-*p*-sulphonyl-α-naphthylamine, prepared by adding benzenediazonium chloride to a well-stirred alkaline solution of the foregoing sulphonamide, was obtained as a viscous sodium salt soluble in dilute alcohol, from which the free azo-compound was precipitated as a brilliant red powder on the addition of $N/2$-acetic acid. Recrystallised from alcohol, this substance was obtained in fine, felted masses of orange-red crystals melting at 203° (Witt., *loc. cit.*, gives 201°). It was readily and completely reduced by the following methods :—

(1) Equal parts of the azo-compound and zinc dust and 5 parts of $2N$-sodium hydroxide solution were heated at 100° in a reduction vessel arranged for rapid stirring in a stream of hydrogen. After fifteen minutes the bright colour of the azo-compound had disappeared, the vessel was rapidly cooled in ice, and the contents filtered without delay into excess of $N/2$-acetic acid, when the base was precipitated as a pale mauve, flocculent solid which was washed with chloroform to remove coloured oxidation products : yield 61 per cent. of theory.

(2) Sodium hyposulphite (4 grams) dissolved in 20 c.c. of water was added to 4 grams of benzene-4-azotoluene-*p*-sulphonyl-α-naphthylamine dissolved in 25 c.c. of $5N$-sodium hydroxide solution diluted with 250 c.c. of water. The solution was warmed at 50—60°, stirred until colourless, and then filtered into dilute acetic acid, the product being crystallised from alcohol.

(3) Ten parts of the azo-compound were dissolved in 40 parts of alcohol diluted with 40 parts of water and containing 1 part of ammonium chloride. To the boiling solution 10 parts of zinc dust were added; the mixture, stirred until the red colour had disappeared, was then filtered into dilute acetic acid.

*Toluene-*p*-sulphonyl-*1 : 4*-naphthylenediamine* crystallised from alcohol in tablets melting at 185—188° (Found: N = 9·07. $C_{17}H_{16}O_2N_2S$ requires N = 8·97 per cent.). Of the three reduction processes the second gave the purest product, although requiring the longest time for completion.

(ii) *Naphthalene-α-sulphonyl-*1 : 4*-naphthylenediamine*, α-$C_{10}H_7$·SO_2·NH·$C_{10}H_6$·NH_2.

Naphthalene-α-sulphonyl-α-naphthylamine (5·75 grams), prepared from naphthalene-α-sulphonyl chloride and α-naphthylamine by the general method [I. (i)], was dissolved in 8·5 c.c. of $5N$-sodium hydroxide diluted with water to 1000 c.c., this naphthalide being very sparingly soluble.

The calculated amount of benzenediazonium chloride was added to the cooled solution with stirring, when a bulky orange precipitate of the azo-compound was obtained: yield 7·5 grams.

The reduction of the azo-compound took place normally, requiring for the above quantity 8 grams of zinc dust and 100 c.c. of 2*N*-sodium hydroxide. The product was a pale mauve powder, m. p. 194° (Found: N = 8·11. $C_{20}H_{16}O_2N_2S$ requires N = 8·04 per cent.).

(iii) *Naphthalene-β-sulphonyl-1:4-naphthylenediamine,*
$\beta\text{-}C_{10}H_7\cdot SO_2\cdot NH\cdot C_{10}H_6\cdot NH_2$.

Naphthalene-β-sulphonyl-α-naphthylamine was first prepared as in the foregoing cases, when a theoretical yield was obtained. The benzeneazo-compound yielded a sodium salt in a much more granular form than the corresponding compound in I. (ii). The free azo-derivative precipitated from alcoholic solution by dilute acetic acid had a dark brick-red colour and melted at 176°.

By using the method and quantities given under I. (ii) this azo-compound was readily reduced and the base precipitated by *N*/2-acetic acid as a pale mauve solid closely resembling its toluenesulphonyl homologue. After washing with chloroform the base melted at 199°: yield 90 per cent. (Found: N = 7·82. $C_{20}H_{16}O_2N_2S$ requires *N* = 8·04 per cent.).

II. *Arylenedisulphonylbis-1:4-naphthylenediamines.*
(*General Formula III.*)

(i) *Benzene-1:3-disulphonylbis-1:4-naphthylenediamine,*
$C_6H_4(SO_2\cdot NH\cdot C_{10}H_6\cdot NH_2)_2$.

Benzene-1:3-disulphonylbis-α-naphthylamine (m. p. 245°) was prepared by grinding two molecular proportions of α-naphthylamine with one of benzene-1:3-disulphonyl chloride and three of fused sodium acetate. Four grams of the product dissolved in 100 c.c. of dilute sodium hydroxide (5 c.c. of 5*N*-sodium hydroxide and 100 c.c. of water) were treated with a diazonium chloride solution prepared from 1·5 grams of aniline. The dark orange azo-compound was reduced with zinc dust and sodium hydroxide as in former cases, and the product was a pale mauve powder which melted at 190—195° (Found: N = 10·95. $C_{26}H_{22}O_4N_4S_2$ requires N = 10·81 per cent.).

(ii) *Naphthalene-2:7-disulphonylbis-1:4-naphthylenediamine,*
$C_{10}H_6(SO_2\cdot NH\cdot C_{10}H_6\cdot NH_2)_2$.

Naphthalene-2:7-disulphonyl chloride and the 2:6-isomeride required in the following preparations were obtained from the

recrystallised sodium salts of the corresponding isomeric 2 : 7- and 2 : 6-disulphonic acids.

Naphthalene-2 : 7-disulphonylbis-α-naphthylamine was obtained as a pale lilac product melting above 250°, the yield being 80 per cent. of the calculated quantity. The dark reddish-brown benzeneazo-derivative of the foregoing compound was reduced as in former cases, although the time required to complete the reaction was rather longer. The product obtained had the characteristic physical properties of the series and did not darken below 300° (Found: N = 9·47. $C_{30}H_{24}O_4N_4S_2$ requires N = 9·86 per cent.).

(iii) *Naphthalene*-2 : 6-*disulphonylbis*-1 : 4-*naphthylenediamine*.

This substance prepared by the general method, was a pale—almost colourless—pink powder, darkening at 150°, intumescing at 165°, and melting at 180° (Found: N = 9·36. $C_{30}H_{24}O_4N_4S_2$ requires N = 9·86 per cent.).

(iv) *Naphthalene*-1 : 6-*disulphonylbis*-1 : 4-*naphthylenediamine*.

Naphthalene-1 : 6-disulphonyl chloride (1 gram) was mixed intimately with 0·9 gram of α-naphthylamine and 0·9 gram of fused sodium acetate, giving a bright orange, almost liquid paste, finally becoming quite hard. This product was ground to powder and warmed cautiously with 10 c.c of 2*N*-sodium carbonate solution, then collected and finally washed with warm water, when it was obtained as a pale lilac-coloured, granular solid. This dissolved with difficulty in 150 c.c. of *N*/5-sodium hydroxide and to the cooled solution was added benzenediazonium chloride from 0·45 gram of aniline. A yield of 2·5 grams of the bright red azo-compound was obtained on the addition of 10 c.c. of 2*N*-acetic acid. The reduction of this substance was brought about readily by dissolving it (2·5 grams) in 5 c.c. of 5*N*-sodium hydroxide and 100 c.c. of water and treating with 3 grams of zinc dust. The reduction was complete in twenty minutes at 100° and the liquid was cooled rapidly and filtered into 50 c.c. of *N*/2-acetic acid, when the base was obtained as an almost white powder darkening slightly when dried, but not melting below 250° (Found: N = 9·27. $C_{30}H_{24}O_4N_4S_2$ requires N = 9·86 per cent.).

(v) *Naphthalene*-1 : 5-*disulphonylbis*-1 : 4-*naphthylenediamine*.

In this preparation it was found to be essential to start from purified naphthalene-1 : 5-disulphonyl chloride.

Twelve grams of commercial "Armstrong salt" (sodium naphthalene-1 : 5-disulphonate) were dried at 110°, mixed with 16 grams of phosphorus pentachloride and 10 c.c. of dry toluene, and the

mixture stirred at 100° for thirty minutes. The crude naphthalene-1 : 5-disulphonyl chloride was purified by extraction with benzene and crystallisation from this solvent. The purified sulphonyl chloride melting at 175° was mixed intimately in a warm mortar with two molecular proportions of *α-naphthylamine* and anhydrous sodium acetate. The resulting naphthalene-1:5-disulphonylbis-α-naphthylamine was coupled in alkaline solution with *benzenediazonium chloride* (2 mols.) and *the azo-derivative was* precipitated completely on adding $2N$-acetic acid. This benzeneazo-compound (Found: N = 11·15. Calc., N = 11·26 per cent.), of which 2·2 grams were obtained from 1 gram of naphthalene-1 : 5-disulphonyl chloride, was reduced with 2 parts of zinc dust and 3 parts of $5N$-sodium hydroxide in 50 parts of water at 100°. The addition of acetic acid to the filtered solution precipitated the mauve diamine, which did not melt below 250° (Found: N = 9·64. $C_{30}H_{24}O_4N_4S_2$ requires N = 9·86 per cent.).

III. *Arylsulphonyl*-1 : 4-*naphthylenediaminesulphonic Acids.*

When the method described above for the condensation of the sulphonyl chlorides with α-naphthylamine was applied to similar experiments in which the *α-naphthylaminesulphonic acids were* used in place of α-naphthylamine, it was found that no perceptible reaction took place, but that on addition of a relatively small quantity of pyridine the condensation proceeded to completion.

(i) 1-*Toluene*-p-*sulphonyl*-1 : 4-*naphthylenediamine*-8-*sulphonic Acid* (*Formula IV*).

Five grams of α-naphthylamine-8-sulphonic acid, 4·3 grams of toluene-*p*-sulphonyl chloride, and 3 grams of fused sodium acetate were ground up intimately in a warm mortar; three drops of pure dry pyridine were added and the trituration continued. A reaction occurred, the brown paste formed was boiled with 20 c.c. of $N/2$-sodium carbonate solution forthwith for ten minutes and the liquid then cooled. The condensation product dissolved to a clear solution.

The benzeneazo-compound was made as in former cases, the benzenediazonium chloride from 1·8 grams of aniline being poured into the foregoing solution, to which 5 c.c. of $5N$-sodium hydroxide solution had been added. The liquid became brilliant scarlet, but no precipitate of *azo-compound could be observed* even when a portion of the coloured liquid was saturated with sodium chloride. The azo-compound was reduced in solution by boiling with 10 grams of zinc dust and 25 c.c. of $5N$-sodium hydroxide and with further

quantities of zinc dust (10 grams) and of $5N$-sodium hydroxide (20 c.c.); the decolorisation of the solution required about one hour, air being excluded by passing hydrogen into the reduction vessel. After cooling, the liquid was filtered into dilute acetic acid, when a fine, yellowish-white precipitate formed. This product, when removed by filtration, washed with a little water and dried, was obtained as a light purple powder, soluble in water (Found: S = 15·43. $C_{17}H_{15}O_5N_2S_2Na$ requires S = 15·45 per cent.).

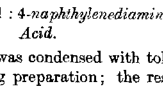
(ii) 1-Toluene-p-sulphonyl-1 : 4-naphthylenediamine-6 (7)-sulphonic Acid.

Commercial Cleve's acid was condensed with toluene-*p*-sulphonyl chloride as in the preceding preparation; the resulting toluene-*p*-sulphonyl-α-naphthylamine-6- and 7-sulphonic acids were converted into benzeneazo-derivatives and these colouring matters were reduced as before, yielding a mixture of the sodium salts of the toluene-*p*-sulphonyl-1 : 4-naphthylenediamine-6- and 7-sulphonic acids.

This mixture and the two preceding compounds were diazotised and the diazo-derivatives mixed with β-naphthol and pyridine; in each case coupling occurred, thus showing that these sulphonic acids were all derived from 1 : 4-naphthylenediamine.

IV. *Arylsulphonyl-1 : 2-naphthylenediaminesulphonic Acids.*

(i) 1-*Toluene*-p-*sulphonyl*-1 : 2-*naphthylenediamine*-4-*sulphonic Acid*,



Five grams of naphthionic acid, 4·3 grams of toluene-*p*-sulphonyl chloride, and 3 grams of fused sodium acetate were ground up in a warm mortar, the reaction being promoted by the addition of two drops of pyridine.

The crude product was boiled with 20 c.c. of $N/2$-sodium carbonate solution and the filtered solution cooled and treated successively with 5 c.c. of $5N$-sodium hydroxide and the diazo-solution from 1·8 grams of aniline. On salting out, a brilliant scarlet precipitate was formed, which tended to coalesce in a viscous mass, but no decomposition was observed. This substance was washed with a little water, warmed to decompose unaltered diazo-compound and then reduced with 10 grams of zinc dust and 50 c.c. of $2N$-sodium hydroxide. When the reduced solution was filtered into dilute acetic

acid, a yellowish-brown precipitate was deposited of *sodium* 1-*toluene*-p-*sulphonyl*-1 : 2-*naphthylenediamine*-4-*sulphonate* (yield 1·1 grams) (Found: S = 15·32. $C_{17}H_{15}O_5N_2S_2Na$ requires S = 15·45 per cent.).

The foregoing reduction was also effected by dissolving the azo-compound in 50 per cent. alcohol and adding an equal weight of zinc dust and one-tenth the weight of ammonium chloride.

(ii) 1-*Toluene*-p-*sulphonyl*-1 : 2-*naphthylenediamine*-5-*sulphonic Acid* (*Formula* V).

Five grams of α-naphthylamine-5-sulphonic acid, 4·3 grams of toluene-*p*-sulphonyl chloride, and 3 grams of fused sodium acetate were ground up in a warm mortar with 1 c.c. of pyridine. The mixture, at first semi-liquid, rapidly stiffened and was finally washed from the mortar with sodium carbonate solution and then boiled for ten minutes. The whole of the residue passed into solution, 10 c.c. of 5*N*-sodium hydroxide were added, and the benzeneazo-derivative was prepared by adding the diazo-solution from 1·8 grams of aniline. The coupling took place rather slowly, but in about half an hour a brick red precipitate had formed. After one hour, salt was added and the mixture left overnight. The dark red precipitate was then reduced with 10 grams of zinc dust and 50 c.c. of 2*N*-sodium hydroxide, and when the red colour had disappeared (thirty minutes) the solution was cooled and filtered into dilute acetic acid, when sodium 1-toluene-*p*-sulphonyl-1 : 2-naphthylenediamine-5-sulphonate was obtained as a pale yellow precipitate.

We desire to express our thanks to the Advisory Council for Scientific and Industrial Research for grants which have partly defrayed the expense of this investigation.

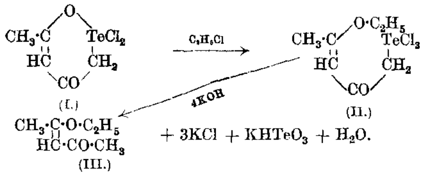
THE CHEMICAL DEPARTMENT,
THE UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, March 7th*, 1921.]

LXVI.—*Researches on Residual Affinity and Co-ordination. Part III. Reactions of Selenium and Tellurium Acetylacetones.*

By GILBERT T. MORGAN and HARRY DUGALD KEITH DREW.

WHEN tellurium tetrachloride and acetylacetone interact in dilute solution in chloroform (B.P.) a yellow substance, $C_7H_{11}O_2Cl_3Te$ (II), is obtained, which owes its origin to the intervention of ethyl chloride

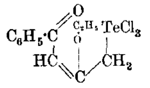
produced by the action of hydrogen chloride on the ethyl alcohol present in the solvent. The compound can also be prepared either by treating tellurium acetylacetone dichloride (I) with ethyl chloride and hydrogen chloride in chloroform solution or by boiling this dichloride with B.P. chloroform saturated with hydrogen chloride.



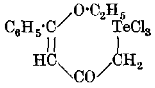
A study of the properties of this additive compound has thrown unexpected light on the constitution of tellurium acetylacetone dichloride and confirms in a direct manner the formulæ for the acetylacetones of tellurium suggested in our former communication on this subject (T., 1920, **117**, 1459). When treated with dilute potassium hydroxide solution the additive compound decomposes quantitatively, giving rise to the *O*-ethyl ether of acetylacetone (III), potassium chloride, potassium tellurite, and water. This reaction not only shows that the additive compound, $C_7H_{11}O_2Cl_3Te$, is tellurium *O*-ethylacetylacetone trichloride (II), but it also supports the cyclic structure (I) advocated for tellurium acetylacetone dichloride.

O-Ethylacetylacetone has been prepared by the action of ethyl iodide on silver acetylacetone, but in this operation the product contains a considerable proportion of *C*-ethylacetylacetone (Curtis, *Amer. Chem. J.*, 1895, **17**, 435). The foregoing reaction should therefore afford a means of preparing in a state of purity the *O*-alkyl ethers of acetylacetone and its homologues. This anticipation has been realised in the following instance. Benzoylacetone condensing with tellurium tetrachloride in chloroform B.P. yields *tellurium* O-*ethylbenzoylacetone trichloride*, transparent yellow prisms (m. p. 140°), which on treatment with alkali hydroxides gives rise to O-*ethylbenzoylacetone*.

The uncertainty attaching to the mode of enolisation of benzoylacetone (Nef, *Annalen*, 1893, **277**, 73; Scheiber and Herold, *Ber.*, 1913, **46**, 1107) extends to the constitution of tellurium *O*-ethylbenzoylacetone trichloride, which may have either of the following configurations :



(IV.)



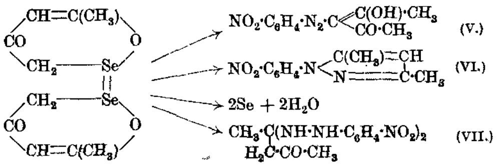
(IVA.)

The results described in the present communication lend support to the former of these formulæ, inasmuch as tellurium *O*-ethylbenzoylacetone trichloride is produced directly from tellurium tetrachloride and benzoylacetone without the intermediate formation of an analogue of tellurium acetylacetone dichloride, a product which arises from acetylacetone and tellurium tetrachloride owing to the possibility, in this case, of the formation of a six-membered heterocyclic ring (formula *I*).

Tellurium acetylacetone, which is prepared most readily by *reducing tellurium acetylacetone dichloride with alkali* hydrogen sulphite (4 mols.) at 0°, combines additively with bromine or iodine in chloroform solution, furnishing respectively *tellurium acetylacetone dibromide* (colourless prisms decomposing at 157—159°) or *di-iodide* (purple red crystals decomposing at 141—143°). These halogen compounds are also available for the synthesis of *O*-alkyl ethers of acetylacetone (compare Ruhemann, T., 1904, **85**, 1180; Claisen, *Ber.*, 1907, **40**, 3909).

The behaviour of selenium acetylacetone towards several aromatic amines and hydrazines has been studied, and the results show that this compound reacts in a characteristic manner towards these bases, selenium being eliminated and acetylacetone derivatives of the bases being produced.

1. *Aromatic Hydrazines.*—The reaction between selenium acetylacetone (1 dimeric molecule) and *p*-nitrophenylhydrazine (2 mols.) has been examined in detail; the organic products are *p*-nitrobenzeneazoacetylacetone (1 mol.) (formula V), 1-p-*nitrophenyl*-3 : 5-*dimethylpyrazole* (VI), and *di*-p-*nitrophenylhydrazinoacetylacetone* (VII).



2. *Primary Aromatic Amines.*—Selenium acetylacetone reacts with one or two molecular proportions of aniline, selenium is

eliminated completely, and 1 : 3-*dianilinoacetylacetone* (VIII) is produced together with oily products.

$$\begin{array}{ll} CO{\cdot}CH_2{\cdot}NH{\cdot}C_6H_5 & CO{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2 \\ HC{\cdot}NH{\cdot}C_6H_5 & HC \\ CO{\cdot}CH_3 & C(OH){\cdot}CH_3 \\ \text{(VIII).} & \text{(IX.)} \end{array}$$

With p-nitroaniline (2 mols.) in alcoholic solution the reaction takes a somewhat dissimilar course. Selenium is set free as before and two organic products arise, namely, 1-p-*nitroanilinoacetylacetone* (IX) and a compound which is probably p-*nitroanilinoethoxyacetylacetone* :

$$\begin{array}{lcl} CO{\cdot}CH_2{\cdot}O{\cdot}C_2H_5 & & CO{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2 \\ HC{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2 & \text{or} & HC{\cdot}O{\cdot}C_2H_5 \\ CO{\cdot}CH_3 & & CO{\cdot}CH_3 \\ \text{(X.)} & & \text{(XA.)} \end{array}$$

In the case of the latter compound the solvent alcohol has taken part in the reaction.

Only one of the foregoing three nitrogenous derivatives of acetylacetone, namely, 1-p-nitroanilinoacetylacetone (IX), retains the *property of forming a copper derivative and of developing a coloration* with ferric chloride.

Selenium acetylacetone in alcoholic solution serves to distinguish the primary and secondary amines from tertiary bases. In the former cases selenium is eliminated on warming gently, whereas this element is not set free by the tertiary bases.

EXPERIMENTAL.

Tellurium O-Ethylacetylacetone Trichloride, $CH_3{\cdot}C(O{\cdot}C_2H_5){:}CH{\cdot}CO{\cdot}CH_2{\cdot}TeCl_3$.

A solution of 7·8 grams of acetylacetone (2 mols.) in 30 c.c. of dry chloroform was added to 10·4 grams of tellurium tetrachloride dissolved in 120 c.c. of the same solvent * and the clear, pale yellow liquid left at the summer temperature for fourteen hours, when a dense orange-yellow oil separated. The mixture was boiled under reflux for one and a half hours, during which period a considerable evolution of hydrogen chloride occurred with a slight separation of tellurium. The resulting liquid was poured from a small amount of dark heavy oil and the chloroform reduced to a few c.c. by evaporation under

* The chloroform used was of B.P. quality dried over calcium chloride for several days and fractionated.

reduced pressure; tellurium acetylacetone dichloride (2·3 grams) separated, and the mother liquor evaporated until an oily product was left, which soon crystallised; this material was spread on porous tile to remove acetylacetone and the solid residue (5·7 grams) was then crystallised successively from chloroform and benzene–light petroleum, when it separated in large, pale yellow, obliquely truncated, tabular prisms melting at 106—107° to a pale yellow liquid from which black tellurium was rapidly deposited (Found: C = 23·61, 23·01; H = 3·15, 3·20; Cl = 29·40, 29·67; Te = 35·34, 35·26. $[C_7H_{11}O_2Cl_3Te]_n$ requires C = 23·28; H = 3·07; Cl = 29·47; Te = 35·32 per cent. The molecular weight by the cryoscopic method in benzene (0·98 gram in 100 grams) was 368; $n = 1$ requires M = 361).

Tellurium O-ethylacetylacetone trichloride is sparingly soluble in cold water with slow decomposition; it dissolves sparingly in ether or carbon tetrachloride, more readily in benzene or chloroform, but is practically insoluble in light petroleum. It crystallises best from carbon tetrachloride or from benzene–light petroleum (40 c.c.: 60 c.c.) but is not recoverable from its solution in acetone. When heated in solvents above 80° it decomposes with elimination of tellurium, and in ordinary benzene this reaction is accompanied by the formation of an intensely blue oil. The purified substance is inodorous and has a somewhat astringent, slightly acidic taste; it gives an acid reaction with blue litmus paper even in dry ether. Cold aqueous potassium bisulphite (3 mols.) liberates tellurium, giving *O*-ethylacetylacetone (partly hydrolysed), potassium chloride, and sulphurous and sulphuric acids. It is readily decomposed by alkali carbonate or hydroxide, yielding *O*-ethylacetylacetone (partly hydrolysed), sodium tellurite, and chloride; it is hydrolysed slowly even by water.

Production of O-*Ethylacetylacetone.*—Twenty grams of tellurium *O*-ethylacetylacetone trichloride were shaken with 12·4 grams of potassium hydroxide (4 mols.), 300 c.c. of water and 300 c.c. of chloroform; heat was generated, a white, amorphous precipitate ($KHTeO_3$) separated, and the chloroform extract after drying over sodium sulphate was fractionated, when 5 grams of *O*-ethylacetylacetone were obtained (b. p. 179—181°/755 mm.). This preparation, which possessed the fragrant odour of crushed dahlias, had the properties ascribed to the *O*-ether by Nef and Curtis (*loc. cit.*), yielded (1) acetaldehyde and acetylacetone on warming with hydrogen peroxide, and (2) *p*-nitrobenzeneazoacetylacetone with *p*-nitrobenzenediazonium acetate. It did not form a semicarbazone with semicarbazide hydrochloride in alcoholic sodium acetate solution, but the semicarbazide was decomposed, yielding hydrazoformamide

NH_2·CO·NH·NH·CO·NH_2, melting at 254° (Found: N = 47·33. $C_2H_6O_2N_4$ requires 47·45 per cent.; compare *Ber.*, 1894, **27**, 57). The *O*-ether was also prepared by Nef's method from ethyl iodide and silver acetylacetone and after removing the *C*-ether by aqueous sodium hydroxide solution, this preparation of the *O*-ether was found to be identical with the product from the tellurium compound. It had a delayed action on ferric chloride and gave no precipitate with aqueous copper acetate solution.

Tellurium O-*Ethylacetylacetone Trichloride from Tellurium Acetylacetone Dichloride.*

1. *Interaction with Ethyl Chloride.*—Powdered tellurium acetylacetone dichloride (2·5 grams) and an ice-cold solution of 4 c.c. of ethyl chloride in 30 c.c. of B.P. chloroform were added successively to 50 c.c. of this solvent saturated with hydrogen chloride at the ordinary temperature. The solid partly dissolved on shaking and passed completely into solution on the water-bath. The transparent orange solution was heated under reflux for half an hour, cooled, treated with 2 c.c. of ethyl chloride, and heated again for one hour. The clear liquid decanted from a drop of dark oil was evaporated under diminished pressure, when a residue of 2 grams was obtained, which speedily solidified and proved to be identical with the foregoing tellurium *O*-ethylacetylacetone trichloride.

2. *Interaction with B.P. Chloroform and Hydrogen Chloride.*—Two grams of powdered tellurium acetylacetone dichloride were heated for one and a half hours under reflux with 80 c.c. of B.P. chloroform saturated with hydrogen chloride. The solid dissolved and the solution, treated as in the foregoing experiment, yielded tellurium *O*-ethylacetylacetone trichloride (m. p. 106°) identical in all respects with the foregoing preparation.

When tellurium acetylacetone dichloride was heated with ethyl chloride and B.P. chloroform alone, the solid dissolved only slowly, and after several hours' boiling, with occasional addition of ethyl chloride, the greater part of the dichloride was recovered unchanged, but a small quantity of tellurium *O*-ethylacetylacetone trichloride was identified. It is evident, therefore, that the reaction is accelerated by the presence of hydrogen chloride, although the gas is not essential to the process.

Ethyl chloride in pure carbon tetrachloride did not lead to any of the *O*-ether, inasmuch as very little tellurium acetylacetone dichloride dissolved even on prolonged boiling.

Tellurium Acetylacetone Dibromide, $C_5H_6O_2$:$TeBr_2$.—This dibromide is obtained most conveniently through the tellurium

acetylacetone dichloride. The latter compound is prepared by the method previously described (T., 1920, **117**, 1462). Attempts to improve this process showed that tellurium tetrachloride and acetylacetone do not interact to form the dichloride in dry ether or carbon tetrachloride, but on adding B.P. chloroform to the reagents in the latter solvent a small yield of tellurium acetylacetone dichloride was obtained, although considerable reduction to metallic tellurium occurred simultaneously.

The reduction of tellurium acetylacetone dichloride to tellurium acetylacetone is greatly facilitated by adding gradually with vigorous shaking powdered potassium bisulphite (4 mols.) to an ice-cold aqueous suspension of the dichloride, when a 90 per cent. yield of tellurium acetylacetone is obtained with only slight elimination of tellurium.

The solubility of tellurium acetylacetone in 100 c.c. of water was 1·6 grams at the boiling point and 0·3 gram at the ordinary temperature; it dissolved more readily in sodium hydrogen carbonate to a yellow solution stable in the cold but decomposed on boiling; the solubility in sodium carbonate was greater, but the solution even less stable on warming.

Tellurium acetylacetone dibromide separated in colourless crystals on adding 0·4 gram of bromine dissolved in 35 c.c. of chloroform to 150 c.c. of chloroform solution containing 0·5 gram of tellurium acetylacetone at 0°. At higher temperatures tellurium was eliminated and a lachrymatory product obtained. When crystallised from chloroform, acetone, ethyl alcohol, or glacial acetic acid, the dibromide separated in colourless prisms which darkened at 129° and intumesced at 159°, giving black tellurium and a lachrymatory oil. When, however, the crystallisation took place from solution in methyl alcohol a new variety of the dibromide separated, which darkened at 120° and intumesced violently at 124°. When crystallised from ethyl alcohol this more fusible variety reverted to the less fusible modification. The latter product was analysed (Found: Br = 41·41. $C_5H_8O_2Br_2Te$ requires 41·47 per cent.).

The existence of two varieties of tellurium acetylacetone dibromide as revealed above led to a re-examination of tellurium acetylacetone dichloride. The latter compound when crystallised from B.P. chloroform or ethyl alcohol separated in prismatic needles, darkened at 155° and decomposed at 169—173° without noticeable intumescence. From methyl alcohol, however, the substance separated in compact, colourless prisms darkening at 140° and decomposing with intumescence at 157°: crystallisation from ethyl alcohol raised the decomposition point of the second variety to 168°, thus indicating

a transformation to the original modification (compare Vernon, T., 1920, **117**, 86, 889).

Tellurium Acetylacetone Di-iodide, $C_5H_6O_2{:}TeI_2$.—The addition of iodine to tellurium acetylacetone was effected in chloroform as in the case of the dibromide. *Tellurium acetylacetone di-iodide* separated in reddish-violet or heliotrope crystals, appearing almost black when massive; the powdered crystals were violet and on heating they blackened at 120° and decomposed somewhat indefinitely at 141—143° (Found: I = 52·31. $C_5H_6O_2I_2Te$ requires I = 52·95 per cent.). This decomposition point was not affected by crystallisation from acetone, but after separating from solution in hot methyl alcohol the di-iodide was obtained in light red crystals which darkened at 114° and decomposed at about 121—126°. Accordingly the di-iodide, like the dibromide and the dichloride, exists in two varieties which in the present case exhibit differences of colour.

The dibromide and the di-iodide are decomposed by alkalis with elimination of halogen and formation of a white, amorphous precipitate soluble in excess; they are reduced to tellurium acetylacetone by cold aqueous potassium bisulphite solution (4 mols.). Unlike the dichloride and the dibromide, the solid di-iodide is at once decomposed, yielding tellurium, when moistened with concentrated hydrochloric acid.

Tellurium O-Ethylbenzoylacetone Trichloride,

$$C_6H_5{\cdot}C(O{\cdot}C_2H_5){:}CH{\cdot}CO{\cdot}CH_2{\cdot}TeCl_3,$$

or $C_6H_5{\cdot}CO{\cdot}CH{:}C(O{\cdot}C_2H_5){\cdot}CH_2{\cdot}TeCl_3$.—Tellurium tetrachloride and benzoylacetone interact in B.P. chloroform, and preliminary experiments showed that the optimum result was obtained with these reagents in molecular proportions. Tellurium tetrachloride (6·4 grams) and benzoylacetone (3·8 grams) were dissolved in 100 c.c. of dry B.P. chloroform, the solution being boiled under reflux for one and a half hours. Hydrogen chloride was continuously evolved, the solution gradually assuming a red colour. The transparent red liquid, decanted from a trace of tellurium and a few drops of yellow oil, was concentrated in a vacuum desiccator until a crystalline product separated. This substance, freed from red impurity by washing with a few c.c. of cold chloroform, was crystallised from chloroform, when the solution, filtered from traces of tellurium and tellurous oxide, yielded pale yellow, transparent crystals. The chloroform mother liquors furnished further crops of this substance, the yield of purified compound being 80 per cent. of the calculated amount. The use of two molecular proportions of the diketone to one of tellurium tetrachloride gave less favourable results even when the proportion

of chloroform was varied; the product was contaminated with unchanged benzoylacetone and a red tar. Purification of the resulting *tellurium O-ethylbenzoylacetone trichloride* was effected by crystallisation from hot chloroform, carbon tetrachloride or benzene, light petroleum being employed to decrease the solubility. Yellow, prismatic tablets were thus obtained darkening at 138° and decomposing at 140° (Found: Cl = 24·83; Te = 30·16. $C_{12}H_{13}O_2Cl_3Te$ requires Cl = 25·15; Te = 30·14 per cent.).

The trichlorides derived from acetylacetone and benzoylacetone do not give immediate colorations with ferric chloride, although the colour is slowly developed.

Tellurium *O*-ethylbenzoylacetone trichloride is somewhat less soluble than the trichloride derived from acetylacetone. It is decomposed by prolonged boiling above 80°, and although very soluble in acetone it is not recoverable from this medium. It is decomposed by hydroxylic solvents and is slowly attacked by moisture, alkalis, and alkali bisulphite. When two parts dissolved in 30 parts of chloroform were shaken with one part of potassium hydroxide (4 mols.) in 10 parts of cold water, an appreciable rise of temperature was observed and a white precipitate (probably $KHTeO_3$) produced. The chloroform extract, dried over sodium sulphate and distilled, yielded *O*-ethylbenzoylacetone as a viscid oil with a pleasant odour of dahlias, but somewhat fainter than that of *O*-ethylacetylacetone.

The *O*-ether gave a delayed action with aqueous-alcoholic ferric chloride solution and did not form a copper salt.

An aqueous-alcoholic solution of hydroxylamine sulphate, *O*-ethylbenzoylacetone, and sodium acetate was warmed on the water-bath until the odour of the *O*-ether disappeared, the liquid was treated successively with sodium hydroxide and mineral acid and extracted with ether. The ethereal extract, evaporated to dryness, left a residue which consisted of phenylmethyl*iso*oxazole and a small amount of benzoylacetone. The latter was removed by dissolving in ether and extracting with aqueous sodium hydroxide solution. The *iso*oxazole obtained from the ether crystallised from light petroleum in colourless needles melting at 69° (Claisen and Lowman gave 67—68°. *Ber.*, 1888, **21**, 1150).

Report on the Crystallographic Characteristics of the Tellurium O-Ethylacylacetone Trichlorides.

1. *Tellurium O-Ethylacetylacetone Trichloride.*—This substance was kindly examined by Mr. T. V. Barker. The crystals are anorthic and exhibit the forms *b*{010}, *m*{110}, *a*{100}, *n*{1$\bar{1}$0}, *c*{001}, and *r*{$\bar{1}$01}, the habit being tabular parallel to *b*{010} and

elongated along the vertical axis, as shown in Fig. 1. Following are the results of measurement of three crystals (the differences between observed and computed angles are given in brackets).

	b(010).	m(110).	a(100).	n(1̄10).	c(001).	r([illegible]).
Azimuth (ϕ) ...	0° 0′	*39° 43′	*86° 24′	137° 11′(−2′)	*98° 34′	262° 3[illegible](−41′)
Polar distance (ρ)	90 0	90 0	90 0	90 0	*16 14	*37 45

The Fedorov angular elements † are :—[010] : [01̄1] = 52° 14′,

Fig. 1.

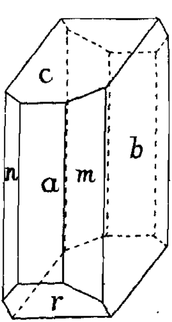
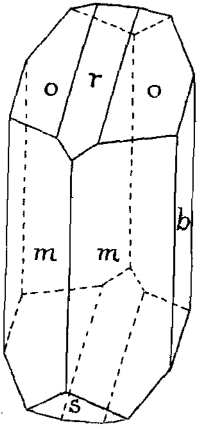


Fig. 2.



† The orthodox (axial-ratio) form of crystal elements does not readily lend itself to the preparation of a gnomonic or stereographic projection in the case of an anorthic or monoclinic crystal, and is therefore of little practical use in crystallography. The above angular elements, consisting of four interzonal angles and one interfacial angle, allow of the preparation of an accurate projection within five minutes' time (as compared with the hour or so involved in the use of axial ratios), and their universal adoption is therefore much to be desired on practical grounds. It will be readily realised that the first and third angles vanish in the special case of the monoclinic system, for the first angle becomes the complement of the second, and the third is necessarily 90°. It must be added that axial ratios can be computed from the angular elements by the simple operation of dividing one sine by another. The converse derivation of angles from axial ratios, on the other hand, is a most tedious and exhausting process. Angular elements are therefore much to be preferred; they possess the additional advantage in principle that they can be actually measured on the two- or

[0$\bar{1}$1] : [001] = 41° 17′, (100) : (010) = 86° 24′, [001] : [$\bar{1}$01] = 36° 41′, [$\bar{1}$01] : [100] = 37° 15′; alternatively, $a : b : c$ = 1·182 : 1 : 1·198, α = 86° 29′, β = 106° 4′, γ = 94° 25′.

Trans., 001/100/010. Complex-symbol, (4h; 16) 49½ (+2; 5,−50).

2. *Tellurium O-Ethylbenzoylacetone Trichloride.*—This substance was also examined by Mr. Barker. The crystals are monoclinic and exhibit the forms m{110}, b{010}, o{111}, r{101} and s{$\bar{1}$01} in the relative proportions illustrated in Fig. 2. Following are the results of measurement of three crystals.

	b(010).	m(110).	r(101).	s($\bar{1}$01).	o(111).
Azimuth (ϕ)	0° 0′	*54° 17′	90° 0′	270° 0′	58° 34′ (+ 8′)
Polar distance (ρ)	90 0	90 0	*47 18	*36 56	51 48 (− 2′)

There is a fair cleavage parallel to m{110}. The angular elements are 56° 35′, 42° 42′, 37° 53′; alternatively, $a : b : c$=0·7288 : 1 : 0·6600, β = 99° 25′.

Trans., $\bar{1}$01/101/010. Complex-symbol, (4d; 6) 55(5).

Reactions of Selenium Acetylacetone.

1. *With* p-*Nitrophenylhydrazine.*—Finely powdered selenium acetylacetone (2·15 grams) and 1·85 grams (2 mols.) of freshly prepared p-nitrophenylhydrazine were mixed in 25 c.c. of absolute alcohol and the mixture heated under reflux on the water-bath for one hour; red selenium separated and p-nitrobenzeneazoacetylacetone was precipitated, the reaction being accompanied by a slight evolution of gas. The azo-derivative and selenium, now changed into the grey variety, were collected and separated by extracting the former product with acetone in a Soxhlet apparatus; the yields of selenium and p-nitrobenzeneazoacetylacetone were 0·93 and 1·2 grams respectively, the corresponding calculated amounts being 0·96 and 1·5 grams. The azo-compound crystallised from glacial acetic acid in lustrous greenish needles, differing in this respect from the orange-brown needles (from glacial acetic acid) or the golden-yellow needles (from acetone) of the preparation obtained from p-nitrobenzenediazonium acetate and acetylacetone. The difference is, however, probably due to a slight contamination of the green form with finely divided selenium. The various, coloured modifications of p-nitrobenzeneazoacetylacetone melted from 219° to 221° and mixtures of these varieties showed no appreciable depression of

three-circle goniometer. No practical objections can be urged against the retention of axial ratios in systems of higher symmetry than the monoclinic, since the all-important angles (the constants actually measured and put to practical use in crystallography) can be readily deduced therefrom with the aid of a table of natural tangents.—(T. V. B.)

melting point. On analysis the green form gave N = 17·07. $C_{11}H_{11}O_4N_3$ requires 16·87 per cent.

The filtrate from selenium and azo-compound was evaporated to dryness, and the soft, orange-red, crystalline deposit was freed from traces of resinous matter by washing with a small amount of cold alcohol; the residue dissolved partly in cold benzene and the filtrate on concentration left almost pure 1-p-*nitrophenyl*-3 : 5-*dimethylpyrazole* (0·5 gram). The final mustard-yellow residue insoluble in benzene was di-*p*-nitrophenylhydrazinoacetylacetone. The yield of pyrazole was only 42 per cent., but in all probability a larger proportion was formed, the loss being due to the difficulty of separating this somewhat fusible and soluble product from resinous impurities. When crystallised from dilute acetic acid the pyrazole separated in characteristic, hair-like, orange-yellow needles felting into woolly masses; it melted at 102° (Found: C = 60·41; H = 5·15; N = 19·85, 19·90. $C_{11}H_{11}O_2N_3$ requires C = 60·81; H = 5·11; N = 19·35 per cent.).

1-*p*-Nitrophenyl-3 : 5-dimethylpyrazole crystallised from alcohol in compact prismatic crystals, very sparingly soluble in water; it gave no red coloration with 5*N*-sodium hydroxide, but dissolved in cold concentrated sulphuric acid to a pale red solution.

Di-p-*nitrophenylhydrazinoacetylacetone*,

$$CH_3{\cdot}C(NH{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2)_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3,$$

the mustard-yellow, sparingly soluble by-product of the foregoing condensation, after being washed with alcohol and warm acetone, sintered on rapid heating at 206° and melted at 218° to a red liquid evolving gas (Found: N = 22·03, 22·25. $C_{17}H_{20}O_5N_6$ requires 21·65 per cent.).

Inasmuch as the two preceding compounds would also arise by the interaction of *p*-nitrophenylhydrazine on acetylacetone, a comparative study was made of this condensation.

p-*Nitrophenylhydrazine and Acetylacetone.*—*p*-Nitrophenylhydrazine (3·3 grams) and 2·1 grams (1 mol.) of acetylacetone in 60 c.c. of absolute alcohol were heated under reflux for half an hour. The boiling solution was filtered forthwith from di-*p*-nitrophenylhydrazinoacetylacetone (1·1 grams) and the cooled filtrate deposited 0·6 gram of this product mixed with the pyrazole. The second filtrate, evaporated to dryness, yielded 2 grams of crude orange 1-*p*-nitrophenyl-3 : 5-dimethylpyrazole, which was purified by successively dissolving in boiling glacial acetic acid and adding hot water, when the compound separated on cooling in the characteristic woolly needles (m. p. 102°).

The di-*p*-nitrophenylhydrazinoacetylacetone crystallised from a large volume of acetone in thin yellow scales, but prolonged boiling

with this or other organic solvents led to the formation of 1-*p*-nitrophenyl-3 : 5-dimethylpyrazole, this change occurring rapidly in glacial acetic acid. On diluting the acetic acid solution with water the pyrazole separated. The mother liquor contained another product even more soluble in dilute acetic acid, which was isolated by concentrating the solution, and purified by crystallisation from boiling ethyl alcohol, when it separated in tough, prismatic, golden-yellow needles sintering at 192° and melting at 206°. This compound, identified as *acetyl*-p-*nitrophenylhydrazine*, was also prepared from *p*-nitrophenylhydrazine by boiling with glacial acetic acid, or by warming with acetic anhydride, being precipitated as before on dilution with water (Found: N = 21·69. $C_8H_9O_3N_3$ requires N = 21·54 per cent.).

2. *With p-Bromophenylhydrazine.*—Selenium acetylacetone (2 grams) and 2·2 grams (2 mols.) of *p*-bromophenylhydrazine were heated together in 50 c.c. of absolute alcohol; a reaction set in on gently warming the solution and after half an hour 0·7 gram of selenium was collected (calculated amount = 0·89 gram). The concentrated filtrate deposited p-*bromobenzeneazoacetylacetone* (0·45 gram), crystallising from acetone, alcohol, or glacial acetic acid in brownish golden-yellow needles melting at 144°. It was identified by preparing another specimen from *p*-bromobenzenediazonium chloride and acetylacetone coupled in presence of dilute aqueous sodium hydroxide solution (96 per cent. yield). This specimen crystallised from ethyl alcohol, benzene, light petroleum, acetone, or glacial acetic acid in lustrous, lemon-yellow needles of lighter hue than the foregoing preparation, which was probably darkened by a trace of selenium. A mixed melting point showed no depression (Found: N = 10·07. $C_{11}H_{11}O_2N_2Br$ requires N = 9·90 per cent.).

3. *With Aniline.*—In benzene solution there was no apparent interaction between aniline and selenium acetylacetone, but in 30 c.c. of absolute alcohol, the selenium compound (2 grams) and freshly distilled aniline (1·2 grams = 2 mols.) interacted slowly in the cold and rapidly on warming, when red selenium was eliminated. After heating under reflux for forty-five minutes the selenium, now transformed into the grey variety, was precipitated quantitatively. The filtrate, which had an odour of phenylcarbylamine, was concentrated in a desiccator, when 0·65 gram of colourless crystals separated (m. p. 130—140°). Repeated crystallisation led to the separation of *dianilinoacetylacetone* in colourless plates melting at 156° (Found: C = 71·84; H = 6·55; N = 9·98. $C_{17}H_{18}O_2N_2$ requires C = 72·31; H = 6·43; N = 9·92 per cent.). This product was also formed, but only in half the above yield, when one molecular proportion of aniline was used in the foregoing decomposition.

Selenium was, however, set free quantitatively and the main product was an oil containing acetylacetone, identified by its *p*-nitrobenzeneazo-derivative.

Dianilinoacetylacetone gave neither a red coloration with ferric chloride nor a copper derivative with copper acetate. On boiling with the latter reagent reduction to cuprous oxide occurred. The dianilino-compound did not dissolve in aqueous alkali hydroxide solutions, but was very sparingly soluble in water.

4. *With* p-*Nitroaniline*.—Six grams (1 mol.) of selenium acetylacetone and 4·68 grams (2 mols.) of *p*-nitroaniline were boiled under reflux in 30 c.c. of absolute alcohol. The selenium, changing from red to grey, during five hours was set free quantitatively (Found: 2·63 grams, calculated 2·68). The alcoholic extract was evaporated to dryness and the residue (7·6 grams) dissolved in boiling alcohol; the filtrate on cooling yielded 6·1 grams of a crystalline mixture, whilst the mother liquor contained unchanged *p*-nitroaniline and resinous matter. The product dissolved in ether (freed from alcohol) was shaken with aqueous copper acetate solution, when a yellowish-green copper derivative *B* was precipitated. The ethereal mother liquor, when dried over sodium sulphate and evaporated, yielded 1·6 grams of a pale yellow compound *A*. This product, crystallised repeatedly from methylated spirit and then from benzene and light petroleum, separated in transparent, very pale yellow prisms or plates and melted at 141°. It gave similar analytical results whether crystallised from alcohol or from benzene–light petroleum (Found: C = 55·45, 55·84; H = 5·87, 6·05; N = 10·46, 10·67, 10·64. $C_{13}H_{16}O_5N_2$ requires C = 55·70; H = 5·76; N = 10·00 per cent.). This substance, which gives analytical numbers corresponding with those of p-*nitroanilino-ethoxyacetylacetone*, was insoluble in cold 5*N*-sodium hydroxide, but on heating it became hydrolysed, yielding *p*-nitroaniline. It did not lose in weight on heating at 100°. When heated on the water-bath for one hour with 4·5*N*-sulphuric acid, *p*-nitroaniline was set free, the other constituent of this hydrolysis being an oil with a pungent odour of pepper. The substance gave no coloration with aqueous-alcoholic ferric chloride solution, and did not form a copper derivative.

1-p-*Nitroanilinoacetylacetone*.—The copper derivative *B*, suspended in ether, was decomposed by 5*N*-sulphuric acid, the ethereal extract yielding 3·1 grams of the product, which, after crystallisation from methylated spirit or from benzene, separated in compact, light yellow prisms melting at 152° (Found: C = 55·62; H = 5·11; N = 12·10. $C_{11}H_{12}O_4N_2$ requires C = 55·91; H = 5·12; N = 11·86 per cent.). This compound, which was more sparingly soluble in organic solvents than the preceding substance *A*, exhibited the

reactions of a 1 : 3-diketone: acidity towards litmus, solubility in aqueous alkali hydroxide solution to a deep red solution, intense but completely fugitive red coloration with alcoholic ferric chloride solution, and a well-defined, yellowish-green copper salt. Dilute mineral acids did not hydrolyse this substance except on long-continued boiling; warming with 5*N*-sodium hydroxide caused a complex decomposition, *p*-nitroaniline and a carbylamine being among the products.

Acetylacetone-p-*nitroanil*, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}C(CH_3){:}N{\cdot}C_6H_4{\cdot}NO_2$, was prepared by heating under reflux acetylacetone (4 grams) and *p*-nitroaniline (1 mol.) in 20 c.c. of absolute alcohol. After one hour the concentrated solution yielded the anil, crystallising from alcohol in intensely bright yellow needles melting at 145° (Found: N = 12·92. $C_{11}H_{12}O_3N_2$ requires N = 12·73 per cent.). This anil was only sparingly soluble in ether, although dissolving readily in chloroform. Its reaction with ferric chloride was delayed, but took place owing to hydrolysis. Unlike the anil from *p*-toluidine, it did not yield a quinoline derivative on treatment with fuming sulphuric acid or acetic anhydride (compare Ferriss and Turner, T., 1920, **118**, 1140).

5. *Interaction of Selenium Acetylacetone and Primary and Secondary Amines*.—When powdered selenium acetylacetone is boiled for a short time in a test-tube with an ethyl-alcoholic solution of a primary or secondary amine, a characteristic red precipitate of selenium makes its appearance. Since tertiary amines do not produce this result, the reaction affords a rapid and convenient method of distinguishing tertiary from primary and secondary amines. In the case of aromatic amines, the presence of strongly acidic groups (such as the nitro-group) causes the elimination of selenium to become much slower, whilst large groups in an ortho-position to the basic group may bring about the same result by steric hindrance. The following are the results of tests with various amines:

Primary Amines.	Secondary Amines.	Tertiary Amines.
Ammonia R.	Methylaniline M.	Dimethylaniline N.
Hydroxylamine R.	Methyl-α-naphthylamine M.	Diethylaniline N.
Aniline R.	Methyl-β-naphthylamine M.	Dimethyl-β-naphthylamine N.
p-Toluidine R.	Benzylaniline S.	Methyl-*p*-toluenesulphonyl-β-naphthylamine N.
p-Nitroaniline M.	Di*iso*amylamine R.	Pyridine (brown precipitate).
α-Naphthylamine R.	Dimethylamine R.	Triethylamine (intense reddish-violet coloration followed by precipitate).
β-Naphthylamine R.	Di*iso*butylamine R.	
α-Aminomethyl-*p*-toluenesulphonyl-β-naphthylamine S.		
β-Nitro-α-naphthylamine S.		
6-Chloro-3 : 4-tolylenediamine R.		

R = rapid reaction; M = fairly rapid reaction;
S = slow reaction; N = no reaction.

The products of these tabulated reactions are under investigation.

The authors desire to express their thanks to the Advisory Council for Scientific and Industrial Research for grants which have partly defrayed the expenses of this investigation.

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LXVII.—*The Soaps as Protective Colloids for Colloidal Gold.*

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ALTHOUGH the soaps in aqueous solution have long been recognised as colloidal in nature, their function as protective colloids does not appear to have been studied very fully. The earliest observation of this property of the soaps is that by Zsigmondy (*Zeitsch. anal. Chem.*, 1901, **40**, 709), who found that sodium oleate and stearate could be regarded as protective colloids by reason of their stabilising action on gold sols. Spring's work (*Kolloid Zeitsch.*, 1909, **4**, 162; 1910, **6**, 11, 109, 164) on the adsorption by soap of soot and other materials is of interest in this connexion, as protection may be regarded as a fundamental problem in adsorption. Gutbier (*Kolloid Zeitsch.*, 1911 *et seq.*) studied a large number of protective colloids but did not include the soaps among them, whilst Hiege's work (*Zeitsch. anorg. Chem.*, 1915, **91**, 145) was confined more or less to the study of a single property of the soaps—the power that they and other protective colloids possess of hindering the growth of gold nuclei, an important factor in gold hydrosol formation.

In view of McBain's recent researches (*J. Amer. Chem. Soc.*, 1920, **42**, 428; T., 1919, **115**, 1279), which have lent much support to his new conception of the soaps, investigations on their colloidal behaviour in various directions become a matter of great importance.

The soaps are considered to function not only as colloids, but also as electrolytes, and as protective colloids for metal hydrosols they might be expected to yield some rather anomalous results; for whilst they may be rich in colloid material possessing the same charge as the metal particles, and therefore favourable to the development of highly disperse sols, the presence of the sodium

or potassium ions completing their electrolytic property would tend in the reverse direction—to bring about coagulation.

As Spring found in the case of soot, there is a maximum concentration of soap which is able to retain the soot in suspension. At higher concentrations the precipitating effect of the sodium ions outweighs the protective effect due to the colloidal soap.

Some investigations have now been undertaken on the behaviour of some typical soaps as protective colloids in gold hydrosol formation. They lend support to these ideas, but hardly corroborate McBain's idea of the transition from colloidal to crystalloidal condition at extreme dilution. At so low a concentration as 0·001 per cent. some of the higher soaps have been found to exhibit protective properties to a remarkable degree.

Experimental.

The soaps used in all these experiments were obtained from Kahlbaum's old stock, or were made from Kahlbaum's pure acids by neutralisation with the theoretical quantity of freshly prepared sodium hydroxide solution. On evaporation to dryness and dissolution in absolute alcohol the latter preparations gave no pink coloration with phenolphthalein. The gold solutions were made from chloroauric acid (recrystallised); their strengths are given in terms of the percentage of gold present.

The reduction of gold chloride by hydrazine hydrate in the presence of starch has been studied very fully by Gutbier (*Koll. Chem. Beihefte*, 1913, 5, 244). It was found that the colour of the gold sols by transmitted light shifted from blue to purple as the concentration of the starch was increased. This is undoubtedly due to the protective action of the starch becoming more prominent at higher concentrations, and shows that gold sols become redder as their degree of dispersity increases. Similar effects have been noted in the case of the soaps, but the procedure adopted was a little different.

With high concentrations of soap it was found more convenient to weigh out definite quantities into test-tubes, to add the requisite amount of water, and to warm until solution took place. After the addition of the gold solution, the mixture was brought to the boiling point, and the reducing agent—a dilute solution of hydrazine hydrate—added. The solutions of lower concentrations of soap (below 1 per cent.) were usually mobile enough to be used with a pipette.

The reduction by hydrazine hydrate is usually completed in a few seconds, but sometimes the sol changes in colour slightly, usually in the direction indicative of increasing dispersity, and probably,

also, of some kind of peptisation. The colours of the sols given in the tables are those, therefore, which were not found to alter on further heating.

TABLE I.

10 *C.c. of* 0·01 *per cent. gold solution reduced with* 1 *c.c. of hydrazine hydrate solution* (1 : 1000).

Concentration of soap.	Colour of sol.	Concentration of soap.	Colour of sol.
None	blue	10% sodium oleate	red
10% Sodium nonoate	,,	2% ,, ,,	,,
5% ,, ,,	purple	0·2% ,, ,,	,,
0·5% ,, ,,	purplish-blue	0·05% ,, ,,	purplish-brown
0·1% ,, ,,	blue	0·02% ,, ,,	brown
10% Sodium laurate	,,	0·01% ,, ,,	blue
5% ,, ,,	purple	10% sodium stearate	red
0·5% ,, ,,	,,	2% ,, ,,	purplish-red
0·1% ,, ,,	blue	1% ,, ,,	,,
5% Sodium palmitate	purple	0·5% ,, ,,	red
2·5% ,, ,,	purplish-red	0·2% ,, ,,	,,
0·12% ,, ,,	purplish-brown	0·05% ,, ,,	purple
0·01% ,, ,,	blue	0·02% ,, ,,	brown
		0·01 % ,, ,,	blue

TABLE II.

10 *C.c. of* 0·1 *per cent. gold solution reduced with* 1 *c.c. of hydrazine hydrate solution* (1 : 400).

Concentration of soap.	Colour of sol.
None	blue, brownish-red by reflected light. Gold flocculates out.
5 Per cent. sodium laurate	,,
5 ,, ,, sodium palmitate	,,
2 ,, ,, sodium oleate	wine-red
1 ,, ,, ,, ,,	,,
0·2 ,, ,, sodium stearate	blue
2 ,, ,, ,, ,,	wine-red
1 ,, ,, ,, ,,	,,
0·2 ,, ,, ,, ,,	blue

TABLE III.

10 *C.c. of* 0·005 *per cent. gold reduced with* 1 *c.c. of hydrazine hydrate solution* (1 : 2000).

Concentration of soap.	Colour of sol.
None	purplish-blue
5 Per cent. sodium laurate	blue
2·5 ,, ,, ,, ,,	purple
0·5 ,, ,, ,, ,,	purplish-red
0·1 ,, ,, ,, ,,	blue
5 ,, ,, sodium palmitate	purplish-blue
2·5 ,, ,, ,, ,,	,,
0·5 ,, ,, ,, ,,	purplish-red
0·1 ,, ,, ,, ,,	brown
0·02 ,, ,, ,, ,,	blue
2 ,, ,, sodium oleate	purplish-red
2 ,, ,, sodium stearate	,,

From these results it is obvious that there is in most cases a maximum concentration of soap which is able to produce a gold sol of the highest degree of dispersity for a given gold concentration. As has been already stated, this is probably due to the presence of the sodium ions which have a coagulating action on the gold sol, and at high concentrations this effect may outweigh that of the protection afforded by the colloidal soap.

Moreover, the alkaline nature of the soap solutions will naturally favour the formation of highly disperse sols at low concentrations, but this alkalinity decreases with increasing concentration, and this is another circumstance militating against high dispersity with high soap concentration.

Other experiments were carried out with varying gold and soap concentrations and also with formaldehyde as reducing agent, but the results obtained merely exemplified the same principles, and for this reason it was not thought necessary to take up space by recording them. Suffice it to say, the soaps differ in one important respect in their behaviour from a protective colloid like zirconium hydroxide, which is positively charged (compare Biltz, *Ber.*, 1902, **35**, 4438). At no particular concentration of gold and soap is it possible to effect mutual precipitation.

Of the soaps examined the most efficient from the point of view of protection appeared to be sodium oleate and stearate, whilst sodium nonoate hardly acted as a protective colloid at all. Protection, then, only becomes pronounced when the colloidal nature of the soaps becomes pronounced.

Now all these conclusions are based upon the assumption that the colours of gold sols are indicative of their degree of dispersity, *and this is where a certain weakness may lie in the general argument. At the same time, the assumption that the red gold sols are more highly disperse than the blue is far more reconcilable with the facts than the reverse assumption, whilst the idea that the colours are indicative of certain differences in the crystalline nature of the gold particles seems, in this case, much more obscure* (compare Steubing, *Ann. Physik.*, 1908, [iv], **26**, 329). The brown sols that are sometimes obtained appear to be intermediate in their degree of dispersity between the blue and the red. Unfortunately, an ultramicroscope was not at the author's disposal, and a more direct confirmation of these conclusions could not be made.

As the soaps themselves are reducing agents for gold chloride, some remarks on this interesting phenomenon will not be out of place. Colloids like gum arabic and starch (Gutbier, *loc. cit.*) are reducing agents, and so also, as Paal found (*Ber.*, 1902, **35**, 2238), are sodium protalbate and lysalbate. In all these cases an assump-

tion must be made that the first stage in the reduction process consists of the formation of an unstable gold salt or gold complex. The breaking up of this gold complex into metallic gold and an organic residue produces the gold hydrosol.

Now it is easy to understand how oxalic acid or sodium oxalate behaves as a reducing agent, as the gold oxalate that is formed can easily decompose into carbon dioxide and metallic gold. Sodium acetate or valerate is a much less efficient reducing agent, probably because of the difficulty of decomposing the corresponding gold salt. But the sodium salts of the higher fatty acids, for example, sodium stearate, palmitate, and even laurate (sodium oleate is a good reducing agent, probably on account of its unsaturated character), were found to be very efficient in this respect, and this is probably on account of their more complex, colloidal nature. The decomposition of the gold salts may readily take place, because the organic residue can easily be absorbed in the colloid-complex. On McBain's theory of the aggregation of ions to form complexes, or on any similar theory, this explanation seems perfectly feasible.

Further experiments were carried out with the ruby-red sols obtained with the aid of sodium oleate and stearate. They were prepared from solutions containing 1 per cent. of sodium oleate or stearate and 0·1 per cent. of gold, and also from solutions containing 0·5 per cent. of sodium oleate and 0·01 per cent. of gold. Reduction took place on heating, but the final stages of the process were effected by dilute hydrazine hydrate solution. Owing to the tendency of the more concentrated solutions to gelatinise, they were diluted to about four times their original volume, and were then dialysed for three days. They were afterwards evaporated nearly to dryness on a water-bath, the final desiccation being effected by sulphuric acid in a vacuum. Such preparations were dark purple, and contained up to 10 per cent. of gold. The author was not able to prepare satisfactory colloids containing much more than this percentage of gold, which indicates the inferiority of the soaps as protective colloids compared with a substance like sodium lysalbate.

The dried solids redissolved in warm dilute alkali solutions to give purple or purplish-red sols, which seemed, on keeping, to be as stable as ordinary soap solutions of the same concentration.

The original ruby-red sols change to blue on the addition of acid, which coagulates the soap. The gold is deposited with the soap when the latter is salted out, for example, with sodium chloride, and the pink colour of the coagulated mass gradually changes through purple to blue. The action of alcohol on these sols is very interesting. When a ruby-red sol is diluted to about

twice its volume with absolute alcohol the colour gradually changes, as before, through purple to blue, sometimes in less than an hour, and the change is accelerated by heating, but there is no coagulation of the soap itself. This is an interesting case of the coagulation of a gold sol by the destruction of the protective colloid responsible for its stability, as the soaps lose their colloidal character in alcoholic solution (Krafft, *Ber.*, 1899, **32**, 1584).

Zsigmondy (*loc. cit.*) found that sodium stearate had as low a gold number as 0·01 at the boiling temperature, whilst sodium oleate gave numbers from 0·4 to 1. Compared with starch and some varieties of gum arabic these numbers are comparatively low, and would suggest that these two soaps were very good protective colloids. Gortner (*J. Amer. Chem. Soc.*, 1920, **42**, 597) redetermined the gold numbers of sodium lysalbate and protalbate, obtaining values from 0·10—0·20, and suggested that the efficiency of these protective colloids was very much overrated. On the whole, therefore, it would seem that Zsigmondy's gold numbers, whilst affording some idea of the protective value of colloids at great dilution, are not altogether indicative of their efficiency as protective colloids in definite colloid preparations.

Hydrazine is a very rapid reducing agent, and, therefore, whilst giving rise to the instantaneous formation of a large number of gold nuclei favourable to the development of the most highly disperse sols, it cannot be diffused throughout the gold solution with sufficient rapidity to produce the maximum effect in this way. At the same time certain important properties of protective colloids are overlooked when this reducing agent is used. By employing sodium oxalate, which is much less rapid in its reducing action, the author has been able to investigate more fully two very important properties of the soaps as protective colloids, (i) the power of hindering the formation of the gold hydrosol by interfering with the function of the gold nuclei as crystallisation centres, a phenomenon studied in another way by Hiege (*loc. cit.*), and (ii) the power of peptising the gold sol from a low to a high degree of dispersity. This reducing agent, however, can only be used with very low concentrations of soap, but the protective properties of the latter are still very pronounced, sometimes at so low a concentration as 0·0001 per cent.

Solutions of the soaps (0·03 per cent.) were prepared by dissolution of the dried substances in water by warming for some time on the water-bath. In most cases the solutions became very cloudy on cooling, and a little sediment was usually deposited after a day or two. It was found possible, however, to use the solutions even after some weeks if they were again warmed on

TABLE IV.

30 C.c. of 0·01 *per cent. gold solution reduced with* 1 *c.c. of* 2 *per cent. sodium oxalate solution.*

Concentration of protective colloid.				Colour change of sol.	Approximate time of sol formation in minutes.
None				*blue*	$2\frac{1}{2}$
0·01	per	cent.	sodium nonoate	,,	3
0·01	,,	,,	sodium laurate	blue to purple	6
0·001	,,	,,	,, ,,	blue	$3\frac{1}{2}$
0·01	,,	,,	sodium palmitate	blue to purple	9
0·001	,,	,,	,, ,,	blue	7
0·01	,,	,,	sodium oleate	purple to purplish-red	5
0·001	,,	,,	,, ,,	blue to purple	11
0·0001	,,	,,	,, ,,	blue	5
0·01	,,	,,	sodium stearate	blue through purple to purplish-red	$5\frac{1}{2}$
0·001	,,	,,	,, ,,	blue to purple	11
0·0001	,,	,,	,, ,,	blue	4
0·01	,,	,,	sodium cerotate	blue through purple to purplish-red	15
0·001	,,	,,	,, ,,	blue	8
0·01	,,	,,	gelatin	purple through purplish-red to red	3
0·001	,,	,,	,,	,,	$3\frac{1}{2}$
0·0001	,,	,,	,,	blue through purple to purplish-red	$4\frac{1}{2}$
0·00005	,,	,,	,,	,,	4
0·00001	,,	,,	,,	blue to purple	$3\frac{1}{2}$
0·000001	,,	,,	,,	blue	$2\frac{1}{2}$

the water-bath, and used immediately on cooling. The lower concentrations of soaps indicated in the tables were made by simple dilution from 0·03 per cent. concentration.

The reduction of the gold solutions was undertaken in batches of 30 c.c. at a time in a 100 c.c. Jena glass beaker, which was so heated that the solutions began to boil in about two and a half minutes. Small variations in the initial temperature of the reduction mixture in each case, due to alteration in the room temperature, did not affect appreciably the results obtained. In order to counteract evaporation losses due to ebullition water was added to the solution from time to time, and in this way it was possible to preserve fairly accurately the initial volume of solution. (The use of a reflux condenser is unnecessary and unsatisfactory, as its presence is inconvenient when the gold solution is being tested.) The reducing agent was added at the moment the beaker containing the gold solution was placed over the Bunsen flame, and the time taken for complete reduction noted. It was very difficult to detect the actual end-point of the reduction, but in the first series of experiments portions of the solutions were tested with hydrazine from time to time to ascertain if any further darkening

in colour would take place. By frequent repetition of the experiments a more satisfactory estimate of the end-points was obtained, but the actual times, as shown in the accompanying tables, cannot be relied upon with very great accuracy. They serve to show in some cases, however, what an enormous effect certain of the soaps have on the time of formation of the gold hydrosol.

The colour change—from blue through purple to red—is undoubtedly due to a peptisation of the colloidal gold, and is the reverse of that found by Zsigmondy and others for the coagulation process.

The behaviour of the soaps in this way, compared with a protective colloid like gelatin, is indicated in the table on p. 631.

Menz (*Zeitsch. physikal. Chem.*, 1909, **66**, 129) found that the protective effect of gelatin increased with decreasing size of the gelatin ultramicrons, and similar effects may be noted in the above table. Both sodium oleate and stearate appear to have a more pronounced effect in hindering the formation of the sol at a concentration of 0·001 per cent. than at 0·01 per cent., probably because at the lower concentration the colloidal soap particles are smaller in size, and may be more strongly adsorbed. This seems quite a feasible assumption, but may not apply so readily to the case of gelatin. The ultramicroscopic character of the gelatin solutions is probably determined by the past history of the original gelatin solution from which they were derived, and subdivision of the particles may not take place so readily on dilution as in the case of the soaps. The power of peptising the sol seems, however, to rest on high concentration of protective colloid, and it does not appear to follow from these results that a concentration of protective colloid which produces the greatest delay in sol formation will also give rise to the most efficient peptisation. Sodium cerotate seems exceptional in this respect, that at a concentration of 0·01 per cent. its peptisation and hindrance effect are both extremely pronounced.

McBain (*loc. cit.*) maintains that at a great dilution both dissociated and undissociated soaps are crystalloids of simple molecular weight, but these results scarcely bear this out. Experiments were therefore carried out in alcoholic solution, where the soaps exist as true crystalloids. Owing to the slight solubility of sodium oxalate in alcohol, solutions containing more than two-thirds their volume of alcohol could not be used in the reduction process, but the small amount of soap present would no longer exist in the colloidal state in such solutions. As will be seen from the following table the soaps as crystalloids are without any protective or peptising action whatever, whilst gelatin, despite the fact that the alcohol

would tend to precipitate it, still retains some of the properties it possesses in truly aqueous solution.

TABLE V.

30 C.c. of 0·01 per cent. gold solution containing 66 (volume) per cent. of alcohol reduced with 1 c.c. of 2 per cent. sodium oxalate solution.

Concentration of the protective colloid.	Colour change in sol.	Approximate time of sol formation in minutes.
None	blue	2½
0·01 per cent. sodium laurate		
,, ,, ,, ,, palmitate		
,, ,, ,, ,, oleate	,,	,,
,, ,, ,, ,, stearate		
,, ,, ,, ,, cerotate		
0·01 ,, ,, gelatin	blue through purple to purplish-red	3
0·001 ,, ,, ,,	blue to purple	3½
0·0001 ,, ,, ,,	blue	3

Whatever alteration the addition of the alcohol produces in the surface tensions of the solutions under investigation, the soaps in the truly molecular condition are evidently not appreciably adsorbed by the gold particles, and cannot function, therefore, as protective colloids. In this condition they resemble sucrose and urea, which are known to be without protective effect. The protective action of soaps in aqueous solntion at great dilution depends, therefore, on their hydrolysis, and it seems reasonable to suppose that the principal product of the hydrolysis is truly colloidal in nature.

Careful conductivity measurements of dilute soap solutions, with and without the addition of colloidal gold (for example, Bredig's pure gold sols) and also, perhaps, cataphoretic measurements, would probably yield some very interesting results, and these might throw much light upon the problem of protection.

Summary.

Some typical soaps have been examined as to their protective action in gold hydrosol formation.

They have been found to exhibit very pronounced protection, but the lower soaps possess the defect that, with increasing concentration, the coagulating action of the sodium ions commences to outweigh the stabilising influence of the colloidal soap.

The protective property is manifest at very great dilution, and it would seem here that the product of the hydrolysis of the soaps is still truly colloidal in nature.

In alcoholic solution, as crystalloids, the soaps are without any protective action.

My thanks are due to Professor Schofield for his friendly advice and encouragement throughout this investigation, and to the Committee of Award of Science Research Scholarships in this State for a scholarship which has enabled me to carry it out.

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UNIVERSITY OF SYDNEY. [*Received, February 17th*, 1921.]

LXVIII.—*The Interaction of Ethylene and Sulphur Monochloride.*

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GIBSON AND POPE (T., 1920, **117**, 271; Eng. Pat. 142875 of 1918) were the first to record with sufficient experimental justification that sulphur monochloride can form additive compounds with unsaturated hydrocarbons; they showed that ethylene is absorbed by sulphur monochloride with formation of ββ′-dichlorodiethyl sulphide and separation of sulphur. By reason of its importance in the preparation of one of the chief materials used in chemical warfare, this reaction has been studied by a number of chemists and many questions of detail have thus presented themselves for discussion and experiment. The above-named workers state that the reaction was best carried out at about 60°, because at that temperature absorption proceeded rapidly, whilst at higher temperatures, with sulphur monochloride of ordinary purity, considerable secondary reaction occurred in which hydrogen chloride was produced with a diminution of the yield of ββ′-dichlorodiethyl sulphide. Later, it was contended by A. G. Green that the product obtained at lower temperatures, namely, at about 30°, is ββ′-dichlorodiethyl disulphide, $(CH_2Cl{\cdot}CH_2)_2S{:}S$, because the atom of sulphur liberated in the reaction does not crystallise out from the absorption product as it does at higher temperatures; in support of this view reference was made to the work of Guthrie (*Quart. Journ. Chem. Soc.*, 1861, **13**, 134) in which he described a compound having the composition last given as contained in the reaction product of ethylene with sulphur monochloride.

A considerable amount of evidence has been adduced

show that the liberated sulphur just above referred to is not in combination as a disulphide, but is merely retained in a state of "pseudo-solution"; the additional evidence on this question brought forward in the present paper seems to prove definitely that the same product, ββ′-dichlorodiethyl sulphide, is formed at all temperatures between 30° and 100° by the interaction of ethylene and sulphur monochloride, and to indicate that the disulphide is an entirely mythical substance. The material which Guthrie obtained by treating sulphur monochloride with ethylene at 100°, and to which he assigned the composition of a dichlorodiethyl disulphide, $(C_2H_4Cl)_2S_2$, and which acts as a feeble vesicant, cannot be obtained as a chemical individual. It is hence impossible to believe that the interaction product of ethylene and sulphur monochloride at 30° is a disulphide identical with Guthrie's disulphide, first, because the former has been now proved to be merely a solution of sulphur in the monosulphide, secondly, because the latter apparently does not exist.

Whilst Gibson and Pope expressed the absorption of ethylene by sulphur monochloride by equation (1) as a direct interaction of the two constituents yielding ββ′-dichlorodiethyl sulphide with separation of sulphur, Conant, Hartshorn, and Richardson have supposed that the reaction occurs between sulphur dichloride, present as a dissociation product of the monochloride, and ethylene, giving an intermediate compound of the constitution $CH_2Cl{\cdot}CH_2{\cdot}SCl$, which later interacts with a further quantity of ethylene to yield ββ′-dichlorodiethyl sulphide. We show in the present paper that the latter compound is formed in the quantities required by equation (1) even during the early stages of the reaction; the mechanism proposed by Conant and his collaborators is thus not in accordance with the facts.

Different workers on this subject have obtained very different yields of ββ′-dichlorodiethyl sulphide by the interaction of ethylene and sulphur monochloride; Gibson and Pope obtained yields up to 98 per cent. of theory, whilst the American workers obtained only about 80 per cent. The explanation of the discrepancy is given in the present paper; when pure ethylene is absorbed by highly purified sulphur monochloride at 60°, the yield is in the neighbourhood of 80 per cent. of theory, but when the ethylene carries a small amount of alcohol vapour the yield rises to 99 per cent. of theory. Insufficient scrubbing of the ethylene prepared from alcohol was thus responsible for the high yields.

Since Gibson and Pope always obtained a high yield, they did not observe the formation of a by-product of high boiling point, which is produced when the low yields are obtained by the use of

ıre materials. Conant and his co-workers observed the occurnce of considerable amounts of this substance, which they conlered to be probably ββ′-dichlorodiethyl pentasulphide, but were ıable to isolate; we have separated the by-product in a state of ırity and find it to be a crystalline ββ′-dichlorodiethyl trisulphide, hich is oxidised by cold nitric acid to β-chloroethanesulphonic id.

Experimental.

Sulphur Monochloride.

The statement is current that sulphur monochloride is a welllefined, stable substance (Fawsitt, *J. Soc. Chem. Ind.*, 1886, **5**, 38), and the compound is generally purified, even when required or determination of physical constants (Kopp, *Annalen*, 1858, **95**, 35), by distillation under ordinary pressures. Thorpe remarked, ıowever (T., 1880, **37**, 356), on distilling sulphur monochloride *with addition of sulphur, that the first runnings are red*; since pure sulphur monochloride is pure yellow in colour, whilst the dichloride is dark red, the partial dissociation of the monochloride into dichloride and sulphur which occurs on heating is readily detected.

Pure sulphur monochloride is conveniently prepared by the following method. The technical material is distilled under ordinary atmospheric pressure with addition of sulphur and about 1 per cent. by weight of highly absorbent charcoal, the latter having been shown (Pope and Heycock, Eng. Pat. 142879 of 1918) to act as a catalyst in a system consisting of sulphur, chlorine, and the sulphur chlorides. The fraction which distils above 137° is redistilled with addition of sulphur and absorbent charcoal under 11 mm. pressure, when pure sulphur monochloride distils at 40° and condenses as a golden-yellow liquid; the first runnings are usually rejected, although this is probably unnecessary. Analysis shows the product to have the composition S_2Cl_2, and its colour, free from any tinge of red, is taken to indicate its freedom from higher chlorides of sulphur.

On heating sulphur monochloride at 60° its colour darkens considerably, and the red tint acquired deepens as the temperature is raised to the boiling point; on cooling, the colour becomes rather lighter, but the pure yellow colour of the original preparation is not regained even after many weeks' standing. When this feebly red-tinted material is treated with absorbent charcoal the colour immediately reverts to the original pure yellow. Sulphur monochloride thus undergoes slight dissociation into sulphur dichloride and sulphur when heated, and, in the absence of a catalyst such as

charcoal, the re-establishment of equilibrium proceeds very slowly after cooling. Whilst it is thus shown experimentally that a system consisting of the components S_2Cl_2, SCl_2, and S can retain its red colour for a long time in the absence of a catalyst, it may be expected that one of S_2Cl_2, S, and Cl_2 could preserve a pure yellow colour for some length of time under similar conditions; in fact, Aten has shown (*Zeitsch. physikal. Chem.*, 1906, **54**, 72) that solutions of chlorine in sulphur monochloride remain pure yellow for some little time. Since the establishment of equilibrium can be aided catalytically, it follows that the greater the purity of the components of the system the more sluggishly will the spontaneous establishment of equilibrium proceed.

The work described in the present paper has been carried out upon sulphur monochloride of which the purity has been assured by the method of preparation just described.

Mechanism of Reaction between Ethylene and Sulphur Monochloride.

In place of the simple equation,

$$(1)\quad 2CH_2{:}CH_2 + S_2Cl_2 = (CH_2Cl{\cdot}CH_2)_2S + S,$$

by which Gibson and Pope (*loc. cit.*) represented the reaction between ethylene and sulphur monochloride, Conant, Hartshorn, and Richardson (*J. Amer. Chem. Soc.*, 1920, **42**, 585) substitute the following three:

$$(2)\quad S_2Cl_2 \rightleftarrows S + SCl_2$$

$$(3)\quad C_2H_4 + SCl_2 = CH_2Cl{\cdot}CH_2{\cdot}SCl$$

$$(4)\quad C_2H_4 + CH_2Cl{\cdot}CH_2{\cdot}SCl = (CH_2Cl{\cdot}CH_2)_2S;$$

they find evidence favouring their view in determinations of the depression of the freezing point of ββ′-dichlorodiethyl sulphide by partly ethylenated sulphur monochloride, and conclude that reaction (3) is dominant until one molecule of ethylene has been absorbed for each one of sulphur monochloride originally present. We have made many attempts to isolate the hypothetical intermediary compound, $CH_2Cl{\cdot}CH_2{\cdot}SCl$, from the partly ethylenated sulphur monochloride, but hitherto without success. The following quantitative results bear upon this question.

Sulphur monochloride (29·8 grams) was caused to absorb an approximately equimolecular proportion of ethylene (6·5 grams) at 60°; the product was then separated into three fractions by distillation under 11 mm. pressure. The first fraction (15·5 grams), collected at 30—80°, is almost pure sulphur monochloride; the second fraction (15 grams), collected at 96—110°, is fairly pure

ββ′-dichlorodiethyl sulphide melting at 7°; the third fraction (2·3 grams) is a mixture of ββ′-dichlorodiethyl sulphide and trisulphide and distils at 110—190°, whilst a residue (3·8 grams) of almost pure sulphur was obtained. Had reaction occurred in accordance with equation (1), 14·1 grams of sulphur monochloride, 18·4 grams of ββ′-dichlorodiethyl sulphide, and 3·71 grams of sulphur should have been obtained.

Again, ethylene (6·2 grams) was absorbed in an approximately equivalent weight of sulphur monochloride (30·3 grams) at 60°, yielding a product (36·2 grams) with the loss of a small quantity (0·3 gram) of sulphur monochloride by evaporation; a portion of the product (35·2 grams) was then cooled in a mixture of ether and solid carbon dioxide. On filtering through a cooled filter in a suitable apparatus, sulphur monochloride (14·3 grams) passed through and a residue (20·9 grams) of solid ββ′-dichlorodiethyl sulphide and sulphur remained; the residue melted at 3°, so that the ββ′-dichlorodiethyl sulphide was not highly impure. The original partly ethylenated sulphur monochloride (36·2 grams) thus yields sulphur monochloride (14·7 grams) and a mixture (21·5 grams) of ββ′-dichlorodiethyl sulphide and sulphur; according to equation (1) it should have yielded 15·0 grams of the former and 21·3 grams of the latter. A blank experiment showed that sulphur monochloride does not become viscid when cooled in a mixture of ether and solid carbon dioxide.

Notwithstanding the close correspondence between the above results and those indicated by equation (1) given by Gibson and Pope, and their entire incompatibility with equation (3) of Conant and his collaborators, it may be objected that the reaction between ethylene and sulphur monochloride in equimolecular proportion is so interfered with by reaction in accordance with equation (4) that the evidence is not conclusive. The American workers state, however, "that even after 23·8 per cent. of the ethylene had been absorbed, there was no dichlorodiethyl sulphide present in the reaction mixture"; the following results bear upon this question.

Ethylene (3·17 grams), in quantity about one-half that indicated in equation (3), was absorbed in sulphur monochloride (30·35 grams) at 60°, the product (33·3 grams) indicating a small loss (0·22 gram) of sulphur monochloride by evaporation. A portion (32·6 grams) of the product was chilled in a mixture of solid carbon dioxide and ether and filtered on a similarly chilled filter; the sulphur monochloride (21·2 grams) was collected and the mixture of ββ′-dichlorodiethyl sulphide and sulphur (11·4 grams, m. p. + 2·0°) retained on the filter. Hence the total weight of original product (33·3 grams) would yield sulphur chloride (21·7 grams) and the mixture

sulphur and organic sulphide (11·6 grams). Equation (1) indicates that 22·47 grams of sulphur chloride and 10·84 grams of the mixture of sulphur and sulphide should have been obtained, whilst, according to the statements of Conant, Hartshorn, and Richardson none of the latter product should have resulted.

The quantitative data given above have been supplemented by much more of a similar kind, and also by oxidation experiments in which the ββ'-dichlorodiethyl sulphide formed at various stages in the ethylenation of sulphur monochloride was determined by conversion into the solid sulphoxide. It seems superfluous to quote more to prove the fallacy of the mechanism suggested by the American workers for the ethylene–sulphur monochloride reaction.

Whether or not the ββ'-dichlorodiethyl sulphide is formed by the action of ethylene on the sulphur monochloride itself or on the dichloride to which the latter gives rise is not yet settled.

ββ'-*Dichlorodiethyl Trisulphide*, $CH_2Cl{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}CH_2Cl$.

Gibson and Pope (*loc. cit.*) obtained yields of ββ'-dichlorodiethyl sulphide by the action of ethylene on sulphur monochloride representing 90 to 98 per cent. of that indicated by equation (1) above; they remarked that the sulphur remaining after distillation "retained a mere trace of resinous matter." Conant, Hartshorn, and Richardson (*loc. cit.*) obtained only an 80 per cent. yield of ββ'-dichlorodiethyl sulphide and, after distillation, noted that the residue "is a thick, black tar which often contains some elementary sulphur"; their examination of this residue led them to conclude that it consists largely of ββ'-dichlorodiethyl pentasulphide, although they did not isolate this compound. They also obtained a liquid which approximated in composition to the trisulphide.

Gibson and Pope never obtained yields of ββ'-dichlorodiethyl sulphide so low as those recorded by these workers, although the yield is considerably influenced by the degree of purity of the reacting materials; further, we have never obtained a residual black tar which resisted separation into definite components. It is likely that divergencies in yields and products may be traced to differences in the degree of purity of the ethylene and sulphur monochloride used.

It is shown in the present paper that when the product obtained by saturating sulphur monochloride with ethylene under various conditions is distilled under 11 mm. pressure, a large proportion of ββ'-dichlorodiethyl sulphide first passes over and is followed by a less volatile fraction in varying proportion. When the collected higher fractions are redistilled under 5 mm. pressure, about

one-half is at once separated as pure ββ′-dichlorodiethyl sulphide, whilst the remainder may be freed from this substance by repeated fractionation under low pressure and is ultimately obtained as a uniform material which boils at 146·5°/5 mm. This substance solidifies in the condenser and is further purified by spreading on porous plate; this white, crystalline compound is ββ′-dichlorodiethyl trisulphide, which has a faint, persistent odour resembling that of the aliphatic polysulphides and melts sharply at 27° (Found: C = 21·2; H = 3·6; Cl = 32·03; S = 43·59. $C_4H_8Cl_2S_3$ requires C = 21·5; H = 3·6; Cl = 31·78; S = 43·09 per cent.).

When ββ′-dichlorodiethyl trisulphide is melted on a microscope slide and allowed to cool it crystallises very sluggishly, but solidification is hastened by pressing a little solid carbon dioxide on to the cover-slip; long, spear-shaped crystals of weak double refraction, with the plane side often perpendicular to one optic axis of a biaxial material, first appear and gradually become converted into a second modification consisting of minute crystal fragments; the change becomes complete in twelve hours and the form of the dimorphous substance first produced has the lower melting point.

The trisulphide is soluble in the ordinary organic solvents and is oxidised instantly by ice-cold nitric acid to β-chloroethanesulphonic acid and sulphuric acid. The former was usually identified by means of its potassium salt; the trisulphide was treated cautiously with nitric acid while maintained at 0°, and after the oxidation, the acid liquid was diluted, carefully neutralised with potassium hydroxide, and evaporated to dryness. The mixed salts so obtained were dried over phosphoric oxide and then refluxed with absolute alcohol; the solution was filtered hot and allowed to cool, when potassium β-chloroethanesulphonate was deposited in pure white scales (Found: K = 21·42; C = 13·08; H = 2·3. $C_2H_4Cl{\cdot}SO_3K$ requires K = 21·41; C = 13·14; H = 2·2 per cent.). Since ββ′-dichlorodiethyl sulphide is only oxidised to the sulphonic acid by prolonged boiling with dilute nitric acid, it seems that the constitution assigned above to the trisulphide is to be preferred to any of the alternatives.

Pseudo-solutions of Sulphur in ββ′-Dichlorodiethyl Sulphide.

When ββ′-dichlorodiethyl sulphide is produced by the absorption of ethylene by sulphur monochloride the liberated sulphur is, under certain conditions, retained partly or wholly in solution; the sulphur, for the most part, crystallises out after heating the liquid at 100° and allowing to cool. Much evidence has been adduced to prove that the sulphur so retained in the liquid is in a state c

"pseudo-solution" and is in no way combined with the ββ′-dichlorodiethyl sulphide. Since, however, it is contended by A. G. Green (*J. Soc. Chem. Ind.*, 1919, **38**, 469B) that the liquid consists of ββ′-dichlorodiethyl disulphide, $(CH_2Cl{\cdot}CH_2)_2S{:}S$, a further proof of the non-occurrence of the disulphide may be put forward.

Sulphur monochloride, activated by the addition of 1 per cent. of finely divided iron, was saturated with ethylene at 30°, the sulphur being retained in the liquid state at this temperature; the product melted at 7·0° and a portion (6·10 grams) was introduced into a small distilling flask connected, by a tube, with a bulb acting as a receiver. The system was then evacuated by aid of a Toepler pump and hermetically sealed. The receiver bulb was immersed in liquid air and slow distillation at the room temperature allowed to proceed for nineteen days, the receiver being kept continuously cool in boiling liquid air; at the expiration of this time the apparatus was opened and the distillate found to consist of ββ′-dichlorodiethyl sulphide (3·85 grams) melting at 12·4°. The original reaction product had thus yielded by distillation at the ordinary temperature 75·8 per cent. on theory of ββ′-dichlorodiethyl sulphide, and it is shown elsewhere in this paper (p. 645) that the material obtained at 30° yields only about 70 per cent. of the sulphide; it follows that the disulphide is not present and that the original statement that the sulphur is retained in a state of "pseudo-solution" in ββ′-dichlorodiethyl sulphide is correct.

The melting point of ββ′-dichlorodiethyl sulphide is depressed by small quantities of substances which are apparently often present as impurities and are retained with tenacity; the highest value we have observed, which is higher than any previously recorded, is 14·2° as the temperature at which the crystalline compound melts completely.

The Absorption of Ethylene by Sulphur Monochloride.

In order to obtain information bearing upon the causes of the differences in yield of ββ′-dichlorodiethyl sulphide and in the character of the product noted by various workers, it seemed desirable to bring about the absorption of ethylene by sulphur monochloride of undoubted purity under precisely similar conditions of stirring; the effect of changes of temperature and of the addition of various foreign agents could then be observed. The sulphur monochloride, about 30 grams in each experiment, was contained in a set of absorption bulbs which were kept agitated by an electric motor running at a constant speed and were main-

tained at a constant temperature in a water-bath. The ethylene used, prepared by the action of alcohol vapour on hot pumice saturated with syrupy phosphoric acid, was of 98 to 99 per cent. purity; it was freed from alcohol by long preservation over water in a gasometer, and was dried before use by passing through tubes filled with pumice soaked in sulphuric acid. Efficient methods were adopted for measuring the volume of ethylene passing into the sulphur monochloride and the volume escaping unabsorbed, so that the amount taken up by the sulphur chloride could be ascertained with considerable accuracy. In every case the ethylene was passed in at such a rate that the speed of exit of unabsorbed gas was kept practically constant.

After saturating the known weight of sulphur monochloride with ethylene, the absorption bulbs were weighed so that, since the absorbed ethylene had been measured under standard conditions, the slight loss of sulphur monochloride by volatilisation with the escaping ethylene could be determined. The melting point of the reaction product was determined and the major portion weighed into a distilling flask and distilled under 12 mm. pressure in a very slow current of dry air; the fraction which distilled at 100—110° under this pressure was reckoned as pure ββ′-dichlorodiethyl sulphide, as indicated by its melting point. After this had passed over, the temperature was raised and a fraction collected at 110—180°/12 mm., which was noted as the intermediate fraction; this contained, as above shown, ββ′-dichlorodiethyl trisulphide together with a considerable proportion of the monosulphide. The residue in the distilling flask was almost pure sulphur and was weighed in each case.

The yield of ββ′-dichlorodiethyl sulphide was calculated as the percentage on that which should have been obtained from the weight of ethylene actually absorbed. Since a small amount of the monosulphide distils with the intermediate fraction, the stated yields are a little too low; they are, however, strictly comparable amongst themselves. The appended table summarises the more important of the results obtained and states the different catalytic agents used.

Several remarkable conclusions now become obvious. In all the experiments made at 60° or 61° with pure sulphur monochloride and ethylene, with the addition of all foreign agents excepting alcohol, the product is a pale yellow liquid which only deposits sulphur after a very considerable time; it appears that with an efficient temperature control the ββ′-dichlorodiethyl sulphide retains the extra sulphur in a state of "pseudo-solution" at temperatures up to 60°. Further, the interaction of pure sulphur monochloride

	1	2	3	4	5	6	7	8	9	10	11	12	13
S_2Cl_2 taken (grams)	29·0	29·9	30·15	30·0	30·0	29·8	29·8	29·9	30·0	30·1	29·8	30·1	30·3
C_2H_4 absorbed (grams)	11·3	11·7	11·75	11·8	11·9	11·85	11·75	11·7	11·8	11·2	12·15	11·3	11·15
Temperature	61°	61°	60°	60°	60°	61°	61°	60°	60°	60°	61°	30°	100°
Catalyst used	none	none	0·488 gram Alcohol	0·949 gram Alcohol	0·3–0·4 gram Alcohol	5% $\beta\beta'$-Di-chloro-diethyl sul-phide	5% $\beta\beta'$-Di-chloro-diethyl sul-phide 0·001 gram Fe	0·3 gram $SOCl_2$	0·3 gram SO_2Cl_2	0·18 gram water	5% $\beta\beta'$-Di-chloro-diethyl sul-phide 0·3% Cl	0·015 gram Fe	none
Deposition of Sulphur	Trace in 3 months	Trace in 3 months	Little after 1 day	Copious after 1 day	Deposit during absorp-tion	Trace in 3 months	none after 3 months	none	none	none	none	none	Im-medi-ately on cool-ing
Weight analysed (grams)	27·8	28·1	28·9	31·9	31·8	34·0	35·9	32·1	32·4	33·25	36·0	33·25	17·20
of m. p.	6·8°	6·8°	8·5°	9·0°	9·2°	6·0°	7·0°	7·2°	0·6°	7·0°	5·9°	2·2°	8·0°
Sulphide obtained (grams)	18·1	18·0	19·85	23·3	24·45	22·5	23·6	20·8	20·3	21·6	23·4	19·4	13·25
of m. p.	14·0°	14·0°	13·2°	13·3°	13·0°	13·7°	13·4°	13·8°	13·4°	13·8°	13·8°	12·0°	13·0°
Intermediate obtained	4·5	3·85	3·25	2·5	0·7	5·0	5·9	5·1	6·4	4·7	0·9	8·0	1·4
Sulphur obtained	5·2	6·3	4·95	5·9	5·6	5·2	5·65	5·7	5·15	6·4	5·4	5·05	1·0
Sulphide } Percentage on	78·5	79·1	84·3	90·5	98·8	80·2	83·3	79·1	75·1	78·5	79·5	68·2	90·4
Sulphur } Theory	110·0	131·2	104·3	116·3	111·4	98·4	104·1	106·7	94·5	116·2	96·2	88·2	103·5
Time in hours	7·5	7·5	5·5	5	5	4·5	3·5	6·5	9·0	6·5	4·5	18	3

and ethylene at 60° gives a poor yield of ββ′-dichlorodiethyl sulphide, namely, 78 to 79 per cent. of that required by equation (1); this is in agreement with the results obtained by Conant, Hartshorn, and Richardson (*loc. cit.*, p. 592), who obtained a yield of only 80 per cent. on theory. This low yield of ββ′-dichlorodiethyl sulphide is accompanied by a high yield of the intermediate fraction from which we have separated the trisulphide.

The discrepancy between these results and those of Gibson and Pope (*loc. cit.*), who obtained almost theoretical yields of ββ′-dichlorodiethyl sulphide, is striking, and we therefore studied the effect of *such impurities as might be present in sulphur monochloride upon* the yield. A small proportion of thionyl chloride (No. 8) added to the sulphur monochloride hastens the absorption but leaves the yield unaltered at 79·1 per cent.; a trace of sulphuryl chloride slightly retards absorption and somewhat reduces the yield (No. 9). The preliminary addition of 5 per cent. of ββ′-dichlorodiethyl sulphide facilitates absorption, as noted by Gibson and Pope, with practically no effect upon the yield (No. 6). The addition of ββ′-dichlorodiethyl sulphide and a trace of iron hastens absorption considerably, and a yield of 83·3 per cent. (No. 7) is obtained. The use of sulphur monochloride containing a small amount of sulphur dichloride, corresponding with an excess chlorine content of 0·3 per cent., with addition of ββ′-dichlorodiethyl sulphide, is without appreciable influence on the yield (No. 11).

Attention was next directed to the effect of possible impurities in the ethylene used, and of these alcohol vapour is of most likely occurrence. The introduction of a small amount (0·488 gram) of alcohol into the passage-way of the pure ethylene increased the yield to 84·3 per cent. (No. 3), and when a larger quantity of alcohol (0·949 gram) was provided in a similar manner the yield rose to 90·5 per cent. (No. 4). In these experiments it was noticed that the whole of the alcohol used was carried forward into the sulphur monochloride during the early stages of the absorption and a continuous supply of alcohol to the ethylene was therefore arranged (No. 5); as before, the alcohol acted as a positive catalyst in increasing the speed of absorption, but the use of ethylene always carrying alcohol vapour raised the yield of ββ′-dichlorodiethyl sulphide to 98·8 per cent. of the theoretical value. In this experiment, and in its repetitions, the intermediate fraction containing the trisulphide becomes a very small one, and a large proportion of the sulphur retained in solution crystallises out on cooling.

It is thus shown that in order to obtain the approximately theoretical yields of ββ′-dichlorodiethyl sulphide and the deposition of the sulphur liberated in reaction (1), as was done by Gibson and

Pope, the retention of a small proportion of alcohol vapour by the ethylene is essential.

The presence of a trace of water vapour in the ethylene slightly hastens the absorption but is without effect upon the yield; this is shown by an experiment (No. 10) in which the ten litres or so of ethylene used were moistened by a continuous supply of water (0·18 gram).

The ββ′-dichlorodiethyl sulphide preparations referred to above were made at about 60°, the temperature which Gibson and Pope found to give the most satisfactory results. On attempting to effect the reaction at 30° absorption occurred so slowly that the introduction of a catalyst, in the form of 0·005 gram of iron, was found desirable; the reaction then required eighteen hours for completion (No. 12), and the yield of ββ′-dichlorodiethyl sulphide was only 68·2 per cent.; at the same time, the intermediate fraction, containing the trisulphide, was twice as large as those obtained at 60°. This result has been repeated several times and shows that much better yields of ββ′-dichlorodiethyl sulphide are obtained at 60° than at 30°.

A. G. Green observed (*loc. cit.*) that, in the absence of iron, ββ′-dichlorodiethyl sulphide is formed in good yield by the action of ethylene on sulphur monochloride at 100°; this result is now confirmed (No. 13) and a yield of 90·4 per cent. was obtained, the absorption proceeding with great rapidity and sulphur being deposited on cooling. This result is only obtained with very carefully purified sulphur monochloride such as that used in the work now described; the material obtained by distillation of the technical product, such as was used by Gibson and Pope, absorbs ethylene with evolution of hydrogen chloride at temperatures above 70° and little or no ββ′-dichlorodiethyl sulphide results.

The more important conclusions to be drawn from the above series of experiments may now be indicated. Highly purified ethylene and sulphur monochloride interact with increasing rapidity as the temperature rises, the speed of interaction being about 1 at 30°, 2·5 at 60°, and 7 at 100°; the yield of ββ′-dichlorodiethyl sulphide is about 70 per cent. at 30°, 80 per cent. at 60°, and 90 per cent. at 100°, whilst the yield of by-product, the trisulphide, is largest at the lower temperature and decreases at the higher temperatures. The addition of preformed ββ′-dichlorodiethyl sulphide or of iron notably increases the speed of reaction, thionyl chloride or water vapour slightly increases the speed of absorption, and sulphuryl chloride causes slow absorption. With all these catalytic agents the sulphur remains more or less indefinitely in " pseudo-solution " and the yield remains about 80 per cent. at 60°.

When a small amount of alcohol vapour is continuously introduced with the ethylene the speed of absorption increases to about 3·5 at 60° and the yield of ββ′-dichlorodiethyl sulphide rises to nearly 99 per cent., whilst the production of the trisulphide falls to a very small amount; at the same time, part of the sulphur crystallises on cooling.

With regard to the speed of the absorption, when ethylene is passed into sulphur monochloride at 60°, the absorption is at first very slow, and does not increase appreciably until about half-way through the period of total absorption, when it assumes a very high and almost constant speed, which falls off quickly towards the end. It should be emphasised that the effect of all the catalysts, both positive and negative, studied in this investigation has been to increase or decrease the initial period of comparatively slow absorption; when this initial period, whether short or long, is over, the absorption continues at a high speed, which is practically the same whatever the catalytic agent present may be.

Guthrie's Dichloroethyl Disulphide.

On filling a large bottle with ethylene, introducing sulphur monochloride, and heating on a boiling-water bath, Guthrie (*loc. cit.*) obtained a product from which, after shaking with water and several times extracting with ether, he separated an oil to which he assigned the composition of a dichlorodiethyl disulphide. Although we have shown that the product of interaction of ethylene and sulphur monochloride at 100° consists of ββ′-dichlorodiethyl sulphide, it seemed desirable to repeat Guthrie's treatment of the material. After sulphur monochloride had been saturated with ethylene at 100° and allowed to cool, a considerable amount of crystalline sulphur separated; the supernatant oil was shaken with warm water, which caused the separation of more sulphur, and was then run off and dried with sodium sulphate. On extraction with ether, viscous sulphur separated as an emulsion and was removed by repeated filtration; the ether solution was then evaporated in a vacuum desiccator, when solid ββ′-dichlorodiethyl sulphide crystallised. Addition of ether to the residue led to the further separation of viscous sulphur and, after filtration, evaporation again led to the crystallisation of the organic sulphide; this melted at 9·7°. No product of the nature of Guthrie's disulphide was obtained.

THE CHEMICAL LABORATORY,
UNIVERSITY OF CAMBRIDGE. [*Received, March 3rd*, 1921.]

LXIX.—*Organic Derivatives of Silicon. Part XXIV.* dl-*Derivatives of Silicoethane.*

By Frederic Stanley Kipping.

The study of the action of sodium on certain mono- and di-halogen derivatives of silicohydrocarbons was commenced some ten years ago, and it was then found that hexaphenylsilicoethane, Si_2Ph_6, could be obtained from phenylsilicon trichloride, whereas phenylethylsilicon dichloride (T., 1907, **91**, 215) gave a product which seemed to be the unsaturated compound, SiEtPh⁚SiEtPh (P., 1911, **27**, 143). These observations pointed to the possibility of utilising reactions of this nature for the investigation of organic derivatives of silicon in various directions, and in 1914 further experiments were made with phenylethylpropylsilicyl chloride (T., *loc. cit.*, p. 218), benzylethylpropylsilicyl chloride (T., *loc. cit.*, p. 723), diphenyldichlorosilicane (T., 1912, **101**, 2113) and other compounds.

From the first two of these chlorides, the silicohydrocarbons dl-*diphenyldiethyldipropylsilicoethane* and dl-*dibenzyldiethyldipropylsilicoethane* were respectively prepared, although the reactions did not take place quantitatively by any means. These two derivatives of silicoethane, $SiH_3{\cdot}SiH_3$, were found to have the general characters of silicohydrocarbons of the type SiR_4. Thus, they are both colourless liquids at ordinary temperatures, give normal molecular-weight results by the cryoscopic method in benzene solution, and, in small quantities, can be distilled under atmospheric pressure without their undergoing appreciable decomposition. Although their molecules contain linked silicon atoms, both silicohydrocarbons are attacked only very slowly, if at all, by boiling aqueous alkalis, and even when they are warmed with a solution of sodium methoxide in methyl alcohol or acetone, no rapid evolution of hydrogen is observed. It is obvious, therefore, that the grouping ⁝Si·Si⁝ is not necessarily unstable towards alkalis and that whether the silicon atoms become separated or not is determined by the nature of the atoms or groups with which they are combined. The behaviour of the two silicohydrocarbons towards concentrated sulphuric acid is widely different, and exactly what might have been anticipated from previous observations with derivatives of silicane. The diphenyl compound, like phenylbenzylethylpropylsilicane (T., 1907, **91**, 223), is readily decomposed by the acid, the phenyl group being eliminated as benzene, doubtless in accordance with the equation

$$SiEtPhPr{\cdot}SiEtPhPr + 2H_2O = SiEtPr(OH){\cdot}SiEtPr{\cdot}OH + 2C_6H_6.$$

The dibenzyl derivative, on the other hand, is sulphonated with very great readiness, just as is benzylethylpropylsilicol (T., 1907, **91**, 727) and is no doubt converted into a mixture of the optically isomeric disulphonic acids of the constitution

$$SO_3H \cdot C_7H_6 \cdot SiEtPr \cdot SiEtPr \cdot C_7H_6 \cdot SO_3H.$$

The preparation of these acids was the most important initial object of this work, because, since the two compounds thus obtained should be optically analogous to *dl*-tartaric acid and *i*-tartaric acid respectively, it was hoped that they could be separated from one another and the *dl*-compound then resolved into its optically active components. The experiments, however, were not carried further than to show that, from the product of sulphonation, it was possible to obtain brucine and *l*-menthylamine salts of a disulphonic acid of the composition given above. Whether these salts were derivatives of the *dl*- or of the *i*-acid, or even mixtures of the two, was not established. As it will take some time to prepare the material and to make the more extended investigation of these acids which the author has in view, the publication of the results obtained some years ago seems to be desirable.

EXPERIMENTAL.

dl-*Diphenyldiethyldipropylsilicoethane*, SiEtPrPh·SiEtPrPh.

A freshly distilled sample of phenylethylpropylsilicyl chloride (T., 1907, **91**, 218) which boiled at about 176—180°/100 mm., was diluted with an approximately equal volume of dried xylene, and a slight excess of the theoretical quantity of sodium added to the solution. No visible reaction occurred until the liquid was heated at its boiling point; the metal then became coated with a blue film, which gradually changed into an almost colourless layer of sodium chloride. The liquid was vigorously shaken from time to time, to detach the crust of sodium chloride from the globules, and after having been boiled intermittently during about twenty hours a portion of the clear solution was found to be free from combined halogen. The solution was then filtered, the residue washed with a little xylene, and the combined filtrate and washings submitted to distillation.

After most of the xylene had passed over, the pressure was reduced to 50 mm. and the following fractions were collected: 1. A portion which passed over between 1[illegible] and 225°, and which formed about 20 per cent. of the whole. 2. A slightly fluorescent liquid collected between 225° and 275°, which formed about 60 per cent. of the whole. 3. A viscous, yellow, oily residue.

The experiment was repeated with another sample of the chloride, but again the crude product distilled over a wide range of temperature, and gave fractions substantially the same as before.

From the two main portions (225—275°/50 mm.), by further fractionation under reduced pressure, there was ultimately obtained a colourless liquid boiling at 265—270°/100 mm. This preparation seemed to be a satisfactory specimen of diphenyldiethyldipropylsilicoethane (Found: C = 74·0; H = 9·6; Si = 16·1, 16·0. $C_{22}H_{34}Si_2$ requires C = 74·4; H = 9·7; Si = 15·9 per cent. Cryoscopic determinations in benzene solution gave M. = 339, 341. Calc., M. = 354.)

The yield of this substance was barely 50 per cent. of the theoretical, and the behaviour of the crude product on distillation was that of a complex mixture. This may have been due to the presence of phenylethylsilicon dichloride and phenylethyldipropylsilicane in the samples of phenylethylpropylsilicyl chloride which were employed, as the preparation of the last-named compound in a state of purity is a matter of considerable difficulty (T., 1907, **91**, 219). It is possible, on the other hand, that the action of the sodium on the monochloride is not restricted to the simple elimination of halogen, as is indicated by the results described below.

dl-*Diphenyldiethyldipropylsilicoethane* is a rather viscous liquid having a faint pleasant aromatic odour; it is specifically lighter than water and only very slightly volatile in steam. It is sparingly soluble in cold methyl alcohol, but dissolves much more freely in the hot liquid, and it is miscible with acetone and most of the common organic solvents in all proportions. It is readily attacked by bromine water, giving a heavy, volatile oil, which is no doubt bromobenzene, and a non-volatile product, which is probably formed by the condensation of dihydroxydiethyldipropylsilicoethane. It is also rapidly decomposed by concentrated sulphuric acid at 100° with evolution of benzene, in which respect it resembles other silicohydrocarbon derivatives which contain a phenyl group. Unlike most of those compounds which contain silicon atoms in direct combination, diphenyldiethyldipropylsilicoethane seems to be very stable towards hot solutions of alkali hydroxides; this is probably due to some extent to its insolubility in the aqueous solutions, but even when it is warmed with a solution of sodium ethoxide in aqueous acetone, no appreciable evolution of hydrogen is observed.

dl-*Dibenzyldiethyldipropylsilicoethane*, $SiEtPr(C_7H_7)\cdot SiEtPr\cdot C_7H_7$.

This compound was prepared from benzylethylpropylsilicyl chloride (T., 1907, **91**, 722) in substantially the same way as the

silicohydrocarbon just described; after having been boiled during about ten hours, the xylene solution gave no reaction for combined halogen.

The crude product seemed to be a complex mixture, and when distilled (30 mm.) about 30 per cent. of the whole passed over between about 135° and 160°. The temperature then rose rapidly and a large fraction (about 55 per cent.) was collected between 160° and 240°, most of which boiled fairly steadily in the neighbourhood of 240°; above this temperature the thermometer again rose rapidly, and about ten per cent. passed over between 240° and 300°, leaving abont 5 per cent. of a dark brown residue.

Further fractionation showed that the portion collected from 135° to 160° contained a considerable proportion of dibenzyl, whereas the main product of the reaction consisted principally of a liquid boiling from 240° to 250° (20 mm.). The latter was again distilled and separated into two portions, boiling at 240—244° and 244—248° respectively (20 mm.).

Both these samples seemed to consist of almost pure dibenzyldiethyldipropylsilicoethane (Found: fraction 240—244°, C = 74·7; H = 9·8; Si = 14·2; fraction 244—248°, C = 75·2; H = 10·0; Si = 14·6. $C_{24}H_{38}Si_2$ requires C = 75·2; H = 10·0; Si = 14·5 *per* cent. Cryoscopic determinations in benzene solution gave M. = 340 [fraction 240—244°] and M. = 362 [fraction 244—248°]. Calc., M. = 380).

These results indicate that the sample boiling at 244—248°/20 mm. was the better sample, and the true boiling point of the compound is probably within these limits.

Since the benzylethylpropylsilicyl chloride which was used in the above described experiment was prepared from benzylethylsilicon dichloride and the latter is easily obtained almost free from dibenzyl, the isolation of a considerable quantity of this hydrocarbon seemed to show that its formation had taken place during the interaction of the metal and the monochloride.

dl-*Dibenzyldiethyldipropylsilicoethane* is a colourless, moderately mobile liquid having a faint, pleasant smell, and is specifically lighter than water. It is only sparingly soluble in cold methyl alcohol, but is miscible with most of the common organic solvents. Like the compound described above, it is relatively very stable towards aqueous solutions of the alkali hydroxides, and even when it is warmed with a methyl-alcoholic solution of sodium methoxide there is no sign of the evolution of gas. It does not immediately decolorise a dilute solution of bromine in carbon tetrachloride, but after some time the colour is discharged and the solution begins to fume. It is not oxidised to any appreciable

extent when it is left in contact with an acidified solution of potassium dichromate.

Sulphonation of dl-*Dibenzyldiethyldipropylsilicoethane.*

A small quantity of the silicohydrocarbon shaken with concentrated sulphuric acid formed a pale yellow emulsion, but when gently warmed on a water-bath during five to ten minutes, this emulsion gave a solution which dissolved completely in cold water. The dilute aqueous solution of the product,neutralised with ammonia, gave on the addition of an aqueous solution of brucine hydrochloride a colourless, pasty precipitate, which, after having been roughly dried, separated from acetone in colourless needles.

A larger quantity of the silicohydrocarbon was shaken with abont 3 volumes of concentrated sulphuric acid, and the emulsion left at the ordinary temperature; after some hours, a portion of the liquid, poured into about 10 volumes of water, gave a perfectly clear solution. Like many of the sulphonic acids of silicohydrocarbons, however, the acid was only sparingly soluble in dilute sulphuric acid, and separated as an oil when larger quantities of the sulphonation product were added to a relatively small volume of water. This oil dissolved completely on the addition of a solution of ammonium hydroxide, but when the solution was of a certain concentration, the ammonium salt separated as an oily layer from the aqueous solution of ammonium sulphate.

On the addition of a solution of brucine hydrochloride in slight excess to the neutral solution of the ammonium salt, a pasty, brucine salt was precipitated as before. This precipitate, when dried, was freely soluble in cold acetone, but it could not be obtained in crystals from the solution.

As it was possible that the altered conditions of sulphonation might have given a product different from the first one—an ortho- instead of a para-sulphonic derivative, for example—the first experiment was repeated with a fresh quantity of the silicohydrocarbon, but again the brucine salt was readily soluble in cold acetone and did not separate from the solution in a crystalline form.

The brucine salt from the last two experiments, when fractionally precipitated from its solution in hot chloroform by the addition of benzene, gave a powdery but somewhat gelatinous product, which was no longer readily and completely solnble in acetone. The portion which was insoluble or sparingly soluhle in this liquid was further fractionated from a mixture of chloroform, benzene, and acetone, and finally obtained as a colourless powder.

This preparation seemed to be the brucine salt of the disulphonic

acid. An air-dried sample lost 5·1 per cent. of water at 100°, and the anhydrous salt gave Si = 4·0 per cent. The formula $\begin{matrix} SiEtPr\cdot CH_2\cdot C_6H_4\cdot SO_3H \\ SiEtPr\cdot CH_2\cdot C_6H_4\cdot SO_3H \end{matrix}, 2C_{23}H_{26}O_4N_2, 2H_2O$ requires H_2O = 5·1 per cent. and the anhydrous salt, *Si* = 4·3 *per cent.*

The anhydrous salt was hygroscopic and on exposure to the air seemed to take up $2H_2O$.

l-*Menthylamine Salt of the Disulphonic Acid.*

As the later preparations of the brucine salt did not crystallise well, an aqueous solution of the ammonium salt was treated with an aqueous solution of *l*-menthylamine hydrochloride until no further precipitate was formed. The pasty product was separated by filtration and washed with water, and then some methyl alcohol was poured on the wet filter containing the wet substance. The first portion of the clear solution which came through deposited beautiful, lustrous crystals, but as filtration continued, these became pasty before the operation had been completed, and the addition of water to the filtrate only precipitated a further quantity of a pasty solid. Unfortunately, these lustrous crystals were not obtained again; their precipitation at one stage of the filtration was probably due to the accidental production of a suitable concentration of aqueous methyl alcohol, which may have brought about a separation of the salts of the *dl*- and the *i*-acids, or even a resolution of the former.

The pasty menthylamine salt was separated, roughly dried, and dissolved in boiling acetone; the cold solution deposited a colourless powder, which was further fractionated from a mixture of acetone and methyl alcohol, and finally from wet ethyl acetate.

The salt thus obtained was doubtless the normal l-*menthylamine* salt of *dibenzyldiethyldipropylsilicoethanedisulphonic acid.* Air-dried samples lost 6·2—6·3 per cent. of water at 100°, and the anhydrous compound gave Si = 6·7 per cent. The formula

$$C_{24}H_{38}O_6S_2Si_2, 2C_{10}H_{21}N, 3H_2O$$

requires H_2O = 6·0 per cent., and the anhydrous salt, Si = 6·7 per cent. The equivalent weight of the salt was also determined by the accurate method previously used in the case of menthylamine sulphobenzylethylpropylsilicyl oxide (T., 1907, **91**, 230). The value obtained was E = 430, the calculated value for the above formula being E = 426·4. This *l*-menthylamine salt was a colourless powder, which under the microscope was seen to consist of fern-like crystals; the anhydrous salt sintered at about 208° and seemed to turn yellow, melting completely at about 220°.

It was readily soluble in cold methyl alcohol, but almost insoluble in dry acetone or ethyl acetate; like so many of the salts of silicosulphonic acids, its solubility was very much greater in wet than in dry organic solvents, and it dissolved quite readily in both acetone and ethyl acetate in presence of a very small proportion of water. A solution of the sodium salt, prepared from the menthylamine salt, seemed to be quite optically inactive; the solution gave precipitates with solutions of *d*-hydrindamine and *d*-methylhydrindamine hydrochlorides, and it is probable that further experiments will lead to a complete separation of the *dl*- and the *i*-acids and to the resolution of the former.

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LXX.—*The Photochemical Reaction between Hydrogen and Chlorine and its Variation with the Intensity of the Light.*

By EDWARD CHARLES CYRIL BALY and WILLIAM FRANCIS BARKER.

IN a recent paper it was suggested by one of us (*Phil. Mag.*, 1920, [vi], **40**, 15) that the observed deviations from Einstein's law of photochemical equivalence might very possibly be due to the re-absorption by the surrounding reactant molecules of the energy radiated during the reaction. According to this law, when a reaction takes place photochemically, the absorption by a molecule of an amount of energy equal to one quantum at its absorbing frequency results in that molecule undergoing reaction, and the number of quanta absorbed and the number of molecules reacting must be equal. A study of many photochemical reactions has, however, shown that except in one case the number of molecules reacting is far in excess of the number of quanta absorbed.

In any photochemical reaction it is obvious that the first stage is the absorption of the light energy, and that the whole can be written

$$A + E = B + E + K$$

where A and B are the reactant and resultant molecules respectively, E is the amount of light energy absorbed, and K is the ordinary observed heat of the reaction. Now the molecule A absorbs the energy E at its characteristic frequency, and the

minimum value of E is one quantum at that frequency. On the other hand, it is evident that the whole of the energy on the right hand side must be radiated at frequencies characteristic of the resultant molecule B, that is to say, the total energy radiated during the reaction must be equal to an integral number of quanta at frequencies characteristic of B. It has previously been shown (*Phil. Mag.*, 1920, [vi], **40**, 1) that the frequencies of any molecule are integral multiples of the frequencies of its atoms, and since the molecules A and B have at any rate some atoms in common it follows that they must have frequencies in common. It was therefore suggested that, whereas Einstein's law must hold if the energy radiated during a reaction is dissipated to the surroundings, the fact that A and B have frequencies in common will result in some of this energy being absorbed by further molecules of A. If the amount thus re-absorbed is sufficiently great, more than one molecule of A will react for every quantum absorbed.

This hypothesis can very readily be put to the test of experiment. In the first place, if the reaction $A \rightarrow B$ is endothermic, that is to say, if K is negative, the total energy radiated during the reaction $(E + K)$ will be small, with the result that Einstein's law is more likely to be obeyed. It is interesting to note that in the photochemical conversion of oxygen into ozone, which is a strongly endothermic reaction, Einstein's law is obeyed within the limits of experimental error.

In the second place, when the reaction is exothermic the amount of the radiated energy that is re-absorbed will depend on two factors. It will depend on the molecular concentration of the reactant molecules when the intensity of the activating light is kept constant, and it will depend on the density of the radiation when the molecular concentration is kept constant. Since the density of the radiation is governed by the number of molecules reacting in unit time, the amount of re-absorption will depend on the intensity of the activating light when the molecular concentration of the reactant molecules is kept constant. It should therefore be capable of experimental proof that the divergence from Einstein's law depends on the concentration of the reactant molecules with constant intensity of light, and on the intensity of the light with constant concentration of the reactant molecules. The fact that the divergence from Einstein's law varies with the molecular concentration under constant illumination has already been proved by Henri and Wurmser (*Compt. rend.*, 1913, **156**, 1012). It has also been shown by Bodenstein and Dux (*Zeitsch. physikal. Chem.*, 1913, **85**, 297) in the photochemical union of hydrogen and chlorine that with constant intensity the velocity

of the reaction varies as the square of the concentration of the chlorine. The velocity is independent of the concentration of the hydrogen, provided that this lies within definite limits. This result is of peculiar interest, since it is known that of the two gases the chlorine alone is activated by the light.

In order to complete the experimental proof it remained to investigate whether the divergence from Einstein's law depends on the intensity of the activating light when the molecular concentration of the reactant molecules is kept constant. We have investigated the rate of formation of hydrogen chloride from a mixture of equal volumes of hydrogen and chlorine in the presence of water. The mixed gases were maintained at constant pressure, and since the hydrogen chloride was absorbed as fast as it was formed, the molecular concentration of the hydrogen and chlorine was constant. The results we have obtained show that the divergence from Einstein's law increases rapidly with increase in the intensity of the activating light.

The mixed gases obtained by the electrolysis of aqueous hydrochloric acid were activated hy exposure to light in a glass vessel which was immersed in water and maintained at constant temperature. The reaction vessel contained about 15 c.c. of water and this water together with the electrolyte had previously been saturated with chlorine and then heated at 100° in order to decompose all volatile nitrogen compounds. The reaction vessel was connected with a delicate water-manometer, by means of which the volume change accompanying the reaction was measured. The measurements were not made until equilibrium had been established between the gases and the water in the reaction vessel. The source of light was a 500 candle-power Pointolite lamp, and a constant current through the lamp was maintained by a suitahle resistance. The light passed through two Nicol prisms and hy varying the angle between these any desired intensity could be obtained. The absolute intensities were not determined since relative intensities were sufficient for the present purpose.

The measurements of the reaction velocity establish three facts, each of which independently supports the hypothesis of the re-absorption by the chlorine molecules of tbe radiated energy. In the first place, it is evident that during the first moment of illumination the reaction must follow Einstein's law. The re-absorption of the radiated energy will then commence, with the result that the reaction velocity will increase. It follows, therefore, that with a constant illumination the velocity of the reaction will at first be small but will increase up to a constant maximum, this constant maximum velocity being determined by the proportion of the

radiated energy that is re-absorbed. We have observed this phenomenon in every single observation made and these were nearly 300 in number. It was originally observed by Bunsen and Roscoe (*Pogg. Ann.*, 1855, **100**, 481), who discussed it as part of the general phenomenon of photochemical induction. Burgess and Chapman (T., 1906, **89**, 1399) showed that if no volatile nitrogen compounds are present there is no period of induction, that is to say, the reaction starts immediately the mixture of gases is illuminated. They, however, observed the increase in the velocity of reaction up to the constant maximum.

Whilst this in itself affords striking support to the hypothesis of re-absorption, the converse is more striking still. When the light is cut off after the maximum rate has been established, equilibrium is very quickly reached. If now the light is again allowed to fall on the mixed gases after a short time has elapsed, the initial velocity will not be the same as it was when the apparatus had not been illuminated, but will be faster, and the same constant rate as before will be reached in a shorter time. In order to reproduce the original curve the gases must remain in the dark for at least twenty minutes. Clearly, therefore, it is necessary to recognise the existence of partly activated molecules which the present hypothesis very obviously demands. This phenomenon was also observed by Bunsen and Roscoe. In view of the important bearing of these results on the hypothesis of the re-absorption of the radiated energy, we feel that little apology is needed for this brief statement of their confirmation.

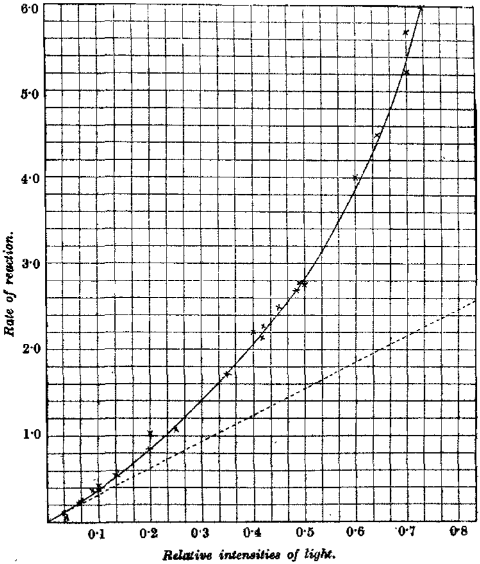
The second phenomenon is the variation in the maximum velocity with the intensity of the light. We have made no quantitative measurements of the light absorbed and therefore have not determined the actual divergence from Einstein's law. This, however is unnecessary, since if Einstein's law is obeyed or if the deviation therefrom is constant the velocity of reaction will be proportional to the intensity of the light. Our measurements show that the velocity increases with the intensity far more rapidly than the simple proportionality requires.

In Fig. 1 the full curve shows a typical relation between the light intensity and the velocity of reaction. On the abscissæ are expressed the relative intensities of the light and on the ordinate the constant maximum velocities. The latter were used, since when they were reached the re-absorption of the radiated energy was maximum. The reaction velocities are expressed in centimetres on the scale of the manometer, and 1 cm. on this scale corresponds with a volume change of 0·0473 c.c.

The reaction velocity at the relative intensity of 0·03 was very carefully determined, seven observations giving the maximum

velocities of 0·11, 0·12, 0·09, 0·11, 0·12, 0·11, and 0·11 cm. on the manometer. The mean of these is 0·11 and this rate is indicated by the point A in Fig. 1. The dotted straight line is drawn from the origin through A and represents the ratio of maximum velocity to intensity which would have been obtained if Einstein's law held

Fig. 1.



or if the deviation therefrom was constant. During the course of this work we encountered considerable difficulty owing to the production of oxygen in the reaction vessel, even although no activating rays fell on the surface of the water. As is well known, the presence of oxygen very materially decreases the velocity of reaction. Many observations were made in which the reaction velocity was considerably less than those on the full curve in Fig. 1

owing to the presence of oxygen, but it is very important to note that in every case these small velocities were always much greater than those read from the dotted straight line.

These results therefore prove without doubt that the deviation from Einstein's law increases with increase in the intensity of the activating light. The shape of the velocity-intensity curve is very interesting, for it shows clearly how the proportion of the radiated energy re-absorbed by the chlorine increases with the intensity. At the highest intensities employed the limit of complete re-absorption is rapidly approached. When this condition is reached the reaction between the two gases, initiated by the absorption of one single quantum by one molecule, will be propagated as an explosion wave through the whole mixture. This criterion of an explosion wave, namely, the complete re-absorption of the radiated energy by the reactant molecules immediately surrounding the locus of the reaction, was defined in the original paper.

The third phenomenon was observed in connexion with the expansion in volume which always takes place when chlorine absorbs light of frequencies lying within its ultra-violet absorption band. In the first place, this expansion was not noticed during the induction period which is always observed when volatile nitrogen compounds are present. In the absence of these compounds the expansion is always observed immediately the activating light falls on the mixture of hydrogen and chlorine. The very interesting observation was made that this expansion is proportional, not to the intensity of the light, but to the rate of the reaction. As has already been explained, the velocity of reaction steadily increases with constant light intensity up to a constant maximum. If the light rays be cut off at any moment the contraction in volume may be measured, and it was found that the expansion first observed and the contraction noted afterwards are proportional to the rate of combination Whatever may be the explanation of this expansion, whether it be due to a dissociation of some of the chlorine molecules into atoms or whether it be a purely thermal effect due to the degradation to heat of the light absorbed, it is obvious that it is increased by the absorption by the chlorine of the energy radiated by the hydrogen chloride. The expansion is observed when the light is deprived of infra-red rays by passage through a layer of water two inches thick, and it is not observed when the ultra-violet rays are removed by interposing a solution of iodine in carbon disulphide. There is thus no doubt that the expansion of the chlorine and its activation are due to the absorption of light of frequencies lying within its ultra-violet absorption band. This band has its centre at $\lambda = 333\ \mu$ and, when the chlorine is at atmospheric pressure, it extends from

about $\lambda = 400\ \mu\mu$ to $\lambda = 270\ \mu\mu$. This band must not be in any way confounded with the fine line absorption which extends through the visible region and to which the visible colour of the gas is due. We have measured the absorptive power of chlorine with the ultraviolet spectrophotometer and find that the extinction coefficient at the centre of the band is 2·5, that is to say, 0·4 cm. of chlorine at atmospheric pressure reduces the intensity of light of wave-length $\lambda = 333\ \mu\mu$ to one-tenth.

The accumulated evidence obtained from these observations undoubtedly very strongly supports the view that the divergence from Einstein's law is due to the re-absorption by the reactant molecules of the energy radiated by the resultant molecules, with the result that many more of the former become activated than would be so activated by the light energy alone. The evidence in support of this explanation would seem to be complete, for it has now been shown that the divergence from the law depends both on the concentration of the reactant molecules under constant illumination and also on the intensity of the light when the concentration of the reactant molecules is kept constant.

It is important to note that similar results have been obtained by Slade and Higson (*Proc. Roy. Soc.*, 1920, [A], **98**, 154) in their experiments with the photographic plate. They find that the amount of silver obtained is not proportional to the intensity of the light. Moreover, it is probable that in the Schwarzschild formula,

$$t_1/t_2 = (I_2/I_1)^p,$$

the value of the constant p varies with the intensity (P. J. Higson, *Photographic Journal*, January, 1921).

These results also lead to two important deductions, first as regards the relation between the frequencies of elementary atoms and their compounds, and secondly as regards the phenomenon of photocatalysis.

Since the radiated energy from the hydrogen chloride is absorbed by chlorine, the frequencies characteristic of the former must be exact integral multiples of the fundamental frequency of the latter. According to the theory of atomic and molecular energy quanta put forward by one of us (*loc. cit.*) an elementary atom is characterised by an elementary quantum of energy associated with a definite physical change, such as possibly the shift of an electron from one stationary orbit to another. The atom can only absorb or emit radiant energy in amounts which are equal to a whole number of its characteristic quanta, and this energy is emitted or absorbed at definite frequencies. These frequencies are determined by the elementary quantum according to the formula quantum/constant =

frequency, where the constant embodies a time factor for the electron shift, assumed to be the same for all atoms and molecules. It may be pointed out that these elementary atomic quanta are very small, the corresponding frequencies being of the order of 3×10^{11}, that is to say, a wave-length of 1000 μ. It is reasonable to suppose that when a compound molecule gains or loses energy as a whole its component atoms share equally in the process. The smallest quantity of energy, therefore, that a molecule can absorb or radiate as a whole will be equal to the least common integral *multiple of the quanta characteristic of its component atoms.* Dr. Norman Campbell has, however, very rightly pointed out that the least common integral multiple of two or more atomic quanta can have no physical significance unless the quanta are integral multiples of a fundamental unit of energy. It may, however, be suggested that all elementary atomic quanta are integral multiples of the quantum characteristic of the atom of hydrogen. Whether this suggestion is true or not, the proof that the frequencies of a compound molecule are exact integral multiples of the frequencies characteristic of its component atoms would undoubtedly afford strong support to the existence of the fundamental unit associated with matter, and hence would justify the principle of the least common integral multiple. The results now communicated show that the frequencies characteristic of the hydrogen chloride molecule are at any rate exact integral multiples of the fundamental frequency of chlorine. It is not possible directly to state that they also prove that the hydrogen chloride frequencies are exact multiples of the atomic frequency of hydrogen, since the reaction between hydrogen and chlorine is catalysed by light of frequencies equal to those of chlorine, light for which hydrogen seems to possess no measurable absorptive power. On the other hand, the probable mechanism of the reaction between hydrogen and chlorine may be considered and it is interesting to note that no attention has been paid to this. A mixture of hydrogen and chlorine undergoes no measurable reaction when screened from light, but when exposed to rays of frequencies comprised within the known ultra-violet absorption band of chlorine the two gases at once begin to unite. The chlorine molecules, inactive in the dark, are activated by the absorption of energy, the minimum amount absorbed per molecule being $9 \times 10^{14} \times 6{\cdot}56 \times 10^{-27} = 5{\cdot}91 \times 10^{-12}$ ergs, where 9×10^{14} is the central frequency of the absorption band. These activated molecules then react with the inactive hydrogen molecules, and it would seem that this process must be accompanied by a transference of energy from the former to the latter. Whatever may be the actual mechanism of the process, the net result is the dissociation

of the hydrogen molecule to form two molecules of hydrogen chloride, and the energy necessary for this dissociation must have been derived from the activated chlorine molecules. This transference of energy can only be possible if the hydrogen and chlorine have frequencies in common, that is to say, either the frequencies of chlorine must be exact integral multiples of the fundamental atomic frequency of hydrogen, or the frequencies of both must be exact integral multiples of a universal fundamental unit. It may be stated, therefore, that the evidence now brought forward is strongly in favour of the exact integral relationship between the molecular frequency of hydrogen chloride and the atomic frequencies of both hydrogen and chlorine. The simplest possible relation is that the molecular frequency of hydrogen chloride should be the least common integral multiple of the atomic frequencies of its component atoms, and it has been shown in previous papers that this relation finds very considerable support in the constant frequency differences between the absorption bands shown by a compound molecule and also between the constituent lines of these bands.

The present results would also seem to have some importance in photochemistry, since they suggest at once the possibility of a new type of photocatalysis. In the case of any reaction, $A + B = AB$, which is known to proceed under the influence of light of a frequency characteristic of A or B, it should be possible to induce the reaction by means of a photocatalyst which absorbs light of a frequency that is not characteristic of either A or B and is therefore not absorbed by either A or B. The criterion of such a catalyst will be that it contains the same elementary atoms as A and B. Since the photocatalyst and the molecules A and B possess the same atoms, they will possess some infra-red frequencies in common. When the photocatalyst is absorbing light of its characteristic frequency, this energy will be radiated in the infra-red, and therefore some of this radiated energy can be absorbed by A and B. If the density of this radiated energy is sufficiently great, the reaction between A and B will proceed, even although the activating light absorbed by the catalyst is not absorbed by either A or B alone. A specific example may be given. It is well known that carbon monoxide and water react to form formaldehyde under the influence of very short wave-length radiation. This radiation is completely absorbed by oxygen, with the result that sunlight has no measurable effect on moist carbon monoxide. It should, however, be possible to catalyse this reaction in sunlight by the use of a substance containing carbon, hydrogen, and oxygen, which selectively absorbs some of the visible or ultra-violet rays present in sunlight. The importance of this type of photocatalysis in the phytosynthetic

processes of the plant is manifest, and experiments are now in progress on these lines.

Again, it is probable that the sensitisation of the photographic plate to red and yellow light by the use of suitable dyes is to be explained on these lines.

It is interesting to note that a typical case of this new type of photocatalysis has just been described by Daniels and Johnston (*J. Amer. Chem. Soc.*, 1921, **43**, 72), who have shown that nitrogen pentoxide has no absorptive power for light of wave-lengths 460—400 $\mu\mu$ and is not decomposed on exposure to light of these wave-lengths. On the other hand, nitrogen pentoxide is decomposed by light of this wave-length when it is mixed with nitrogen peroxide, which is known to have the power of absorbing this light. The authors put forward an explanation which is almost identical with that given above, but they assume that the energy radiated by the nitrogen peroxide in the infra-red can be absorbed by the pentoxide if their absorption bands in that region overlap, and they point out that such overlapping occurs with the short wave infra-red bands of nitrogen pentoxide at 3·39 μ and 5·81 μ, and those of nitrogen peroxide at 3·43 μ and 6·12 μ. This assumption is not satisfactory for two reasons. In the first place, the absorption by the pentoxide of energy radiated by the peroxide cannot take place on the quantum theory unless the frequencies possessed by the two are exactly equal, since otherwise a gain of energy by the system from the surroundings must occur, because the quanta characteristic of nitrogen peroxide at $\lambda = 6·12$ and 3·43 μ are smaller than those characteristic of nitrogen pentoxide at $\lambda = 5·81$ and 3·39 μ. In the second place, it is well known that at low temperatures the breadth of absorption bands decreases until they become a single absorption line. At low temperatures, therefore the overlapping will disappear, and it becomes necessary to postulate that the photocatalysis cannot occur at low temperatures. Such a postulate would mean that the reaction at the ordinary temperature is not purely photochemical, but partly photochemical and partly thermal. On the other hand, since both these oxides contain the same atoms they must possess frequencies in the long wave infra-red which are exactly equal, and doubtless the transference of the energy takes place at these frequencies.

Summary.

1. The photochemical reaction between hydrogen and chlorine at constant concentration has been studied with varying intensity of the activating light.

2. With a given light intensity the amount of hydrogen chloride

formed in unit time is at first small and then rapidly increases up to a constant maximum.

3. The constant maximum rate of formation of hydrogen chloride is not proportional to the intensity of the light. The divergence from Einstein's law of photochemical equivalence depends on the intensity of the light and rapidly increases with the intensity.

4. The expansion of chlorine observed when it is illuminated is proportional, not to the intensity of the light, but to the rate of the reaction.

5. The *divergence from Einstein's law had previously been* suggested as being due to the re-absorption by the reactant molecules of the energy radiated by the resultant molecules. This re-absorption will depend on the concentration of the reactants with constant illumination, and on the intensity of the light with constant concentration. Since the divergence from Einstein's law had already been shown to vary with the concentration under constant illumination, the evidence in favour of the divergence being due to the re-absorption of the radiated energy would now seem to be complete.

6. The results indicate that the frequencies characteristic of the *hydrogen chloride molecule are exact integral multiples* of *both the* fundamental atomic frequency of hydrogen and the fundamental atomic frequency of chlorine. Considerable support is thereby gained for the conclusions drawn from spectroscopic observations that the true molecular frequency of a compound molecule is the least common integral multiple of the atomic frequencies of its component atoms. Such a relation can only hold if a fundamental unit of energy exists, and the suggestion is made that all atomic and molecular energy quanta are integral multiples of the fundamental quantum associated with the hydrogen atom.

7. *A new type of photocatalysis is indicated whereby a reaction* can be photochemically induced by light which is not absorbed by the reactants, but is absorbed by the photocatalyst. This photocatalyst must contain the same elementary atoms as the reactants, and the light which it absorbs is radiated at its characteristic frequencies in the infra-red. Since the photocatalyst and the reactants must have common frequencies in the infra-red, this radiated energy will be absorbed hy the reactants, and if the radiation density is sufficiently great the reaction will proceed.

During the writing of this paper Dr. Norman Campbell has informed us that he discovered some years ago the fact that the reaction between hydrogen and chlorine is not proportional to the intensity of the light. The discovery was not published, but we feel that the confirmation therehy given of the correctness of our

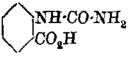
work is very gratifying. We express our cordial thanks to Professor Heilbron for the interest he has taken in the work, and more especially for the suggestion of the application of the new principle of photocatalysis to the phytosynthetic processes of the living plant.

THE UNIVERSITY, LIVERPOOL. *[Received, February 19th, 1921.]*

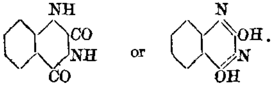
LXXI.—*On some Carbamido-acids and their Hydantoins.*

By JOHN RICHARD SCOTT and JULIUS BEREND COHEN.

URAMIDOBENZOIC (o-carbamidobenzoic) acid, its nitro-derivatives, and also the hydantoin (2 : 4-diketo-1 : 2 : 3 : 4-tetrahydroquinazoline) derived from it were first prepared by Griess (*J. pr. Chem.*, 1872, [ii], **5**, 371),



o-Carbamidobenzoic acid.



Diketotetrahydroquinazoline.

In the course of last year a more careful study of the hydantoin and its derivatives was begun by one of us and the results were prepared for publication, when a paper on the same subject appeared (Bogert and Scatchard, *J. Amer. Chem. Soc.*, 1919, **41**, 2052). As most of our results are embodied in that paper, it is only necessary to refer to the following few additional observations, before discussing the main subject of the present investigation.

Preparation of the Hydantoin from the Carbamido-compound.—6·5 Grams of the carbamido-compound were heated on the water-bath for half an hour with 40 c.c. of concentrated hydrochloric acid (Bogert and Scatchard used sodium hydroxide), yielding 5·5 grams of the hydantoin.

The sodium salt of the hydantoin was obtained by dissolving the latter (2 parts) in a solution of sodium hydroxide (1 part) in water (20 parts). On cooling, clusters of needles separated, which were recrystallised from water. The sodium salt contains $5H_2O$ (not recorded by Bogert and Scatchard) (Found: $H_2O = 33·06$; $Na = 8·04$. Calc. for $C_8H_5O_2N_2Na,5H_2O$: $H_2O = 32·8$; $Na = 8·4$ per cent.).

The Action of Methyl Sulphate.—The dimethyl ether of the hydantoin was prepared by mixing 2 grams of the hydantoin with 3 grams of methyl sulphate, adding sodium hydroxide until alkaline, and warming on the water-bath. This method was used in preference to the action of methyl iodide on the sodium compound. After recrystallisation from boiling water or alcohol, our product melted at 164° (Bogert and Scatchard give 167—168°).

The Action of Sodium Hypochlorite.—A chloroamine derivative, not described by Bogert and Scatchard, was obtained as follows. To 30 c.c. of a 10 per cent. solution of bleaching powder, or the equivalent of sodium hypochlorite, 1 gram of the hydantoin in powder was added and the clear solution then acidified with hydrochloric or acetic acid until no further precipitate was formed. The latter was filtered and washed. The sodium salt was obtained by dissolving the substance in sodium hydroxide solution. The same substance was prepared by dissolving the hydantoin directly in warm sodium hypochlorite solution.

It was analysed by adding potassium iodide solution, acidifying with acetic acid, and titrating the free iodine with sodium thiosulphate (Found: Cl = 18·39. $C_8H_5O_2N_2Cl$ requires Cl = 18·07 per cent.). The substance is probably represented hy one of the following formulae:

$$C_6H_4 < \begin{matrix} CO-NCl \\ NH\cdot CO \end{matrix} \quad \text{or} \quad C_6H_4 < \begin{matrix} CO-NH \\ NCl\cdot CO \end{matrix}.$$

It is very unstable and gradually loses its chlorine when exposed to the air. It is rapidly decomposed when warmed with alcohol, regenerating the hydantoin and at the same time emitting a smell of acetaldehyde.

o-*Acetylcarbamidobenzoic acid*, $NHAc\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2H$, was prepared by heating 0·5 gram of the carbamido-compound with 3 c.c. of acetic anhydride until it just dissolved. On cooling, diluting with water, and making alkaline with ammonia, the acetyl derivative was obtained; it crystallised from dilute acetic acid or alcohol in clusters of felted needles, which sintered at 220° and melted at 225° with effervescence. It dissolved in sodium hydroxide solution, from which it was precipitated by acids.

o-*Benzoylcarbamidobenzoic Acid.*—On heating the carbamido-compound with an excess of benzoyl chloride, the former dissolves, and after a short time the mixture becomes pasty from the separation of the unchanged hydantoin. If, however, the carbamido-compound is dissolved in dilute sodium hydroxide solution and shaken for some time with benzoyl chloride until the smell of the latter disappears, a mass of crystals of the sodium compound of

the benzoyl derivative separates. This is filtered, washed and dissolved in hot water, and, on acidifying, the benzoyl compound separates. It crystallises from boiling water, in which it is moderately soluble, in clusters of long, colourless prisms, which partly melt at about 200°, decomposing into the hydantoin and benzoic acid,

$$C_6H_4<^{NH\cdot CO\cdot NH\cdot CO\cdot C_6H_5}_{CO_2H} = C_6H_4<^{NH\cdot CO}_{CO-NH} + C_6H_5\cdot CO_2H.$$

Carbamidophthalic Acid and its Hydantoin.

3-*Aminophthalic Acid Hydrochloride.*—Thirty grams of finely powdered 3-nitrophthalic acid are added in small portions to a filtered solution of 120 grams of stannous chloride in 300 c.c. of concentrated hydrochloric acid, the mixture being kept cool and each portion being allowed to dissolve before the next is added. The hydrochloride of the amino-acid soon begins to crystallise, and after standing overnight is filtered and washed with a little concentrated hydrochloric acid. After recrystallising from hot concentrated hydrochloric acid, it is dried in a vacuum over sulphuric acid and sodium hydroxide. A little more of the hydrochloride can be obtained by cooling the united filtrates and allowing them to stand. The substance prepared in this way forms a mass of fine, colourless needles, which darken on heating, soften at 210° and melt with evolution of gas at 225°. The free amino-acid may be obtained by gradually adding the hydrochloride to water, in which it is fairly soluble, until the free amino-acid begins to separate, when it is rapidly filtered and the filtrate cooled. After a short time the amino-acid crystallises in colourless needles, which melt at 191—192° with decomposition, forming a yellow liquid.

3-*Carbamidophthalic Acid.*—Twenty grams of 3-aminophthalic acid hydrochloride in powder are dissolved in 200 c.c. of cold water, the solution filtered, and 8 grams of potassium *iso*cyanate in a little water added. The mixture is kept cool by immersion in water, and after standing for half-an-hour, 20 c.c. of concentrated hydrochloric acid added. The carbamido-compound begins to separate as a crystalline precipitate, precipitation being hastened by agitation. After standing for some hours the carbamido compound is filtered, washed with water, and dried in a vacuum *Carbamidophthalic acid* forms a crystalline, greenish-yellow powder melting at 183—185° with decomposition. The yield is 60 per cent of the theoretical. It is insoluble in chloroform, acetone, and light petroleum, and sparingly soluble in alcohol and ether (Found

H_2O = 3·56; N = 11·97, 12·04. $C_9H_8O_5N_2,\frac{1}{2}H_2O$ requires H_2O = 3·87; N = 12·02 per cent.).

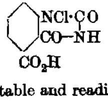
Acetylcarbamidophthalic Anhydride.—One gram of carbamidophthalic acid is heated with 10 c.c. of acetic anhydride; a clear solution is obtained, from which the acetyl compound soon begins to crystallise. After being dried in a vacuum, it melts at 246—247° with decomposition. It does not dissolve in sodium carbonate solution and therefore contains no free carboxyl group.

Hydantoin of 3-Carbamidophthalic acid (*Diketotetrahydroquinazolinecarboxylic Acid*).—Ten grams of carbamidophthalic acid are heated on the water-bath with a mixture of 15 grams of concentrated hydrochloric acid and 10 c.c. of water. The mixture soon forms a colourless, pasty mass. The heating is continued until most of the hydrochloric acid is removed. The mass is then extracted with hot water and the insoluble hydantoincarboxylic acid filtered off, washed with warm water, and dried in a vacuum. The yield is 8·5 grams or 95 per cent. of the theoretical. Thus prepared, the hydantoin is a colourless powder, slightly soluble in alcohol and boiling water; it crystallises from the latter in minute needles, which do not melt below 320°, but sublime slowly above 280°. It dissolves readily in sodium carbonate solution and is reprecipitated by acetic acid (Found: N = 13·28. $C_9H_6O_4N_2$ requires N = 13·59 per cent.).

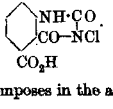
The *sodium* salt is obtained by dissolving the acid in just sufficient hot sodium carbonate solution to give a clear solution. On cooling, the salt crystallises in radiating masses of slender needles. It may be recrystallised from water, in which it is very soluble (Found in air-dried material: H_2O = 19·06; Na = 7·99. $C_9H_5O_4N_2Na,3H_2O$ requires H_2O = 19·15; Na = 8·16 per cent.).

Action of Sodium Hypochlorite on the Hydantoin.

The hydantoin dissolves in sodium hypochlorite solution with a brown colour, and from the solution acetic acid throws down a colourless precipitate, which is filtered, washed with water, and dried in a vacuum. The substance liberates iodine from potassium iodide, and when heated with alcohol loses chlorine, regenerating the original substance. It is therefore probably represented by one of the following formulæ or the tautomeric forms:



or



It is very unstable and readily decomposes in the air. On titrating

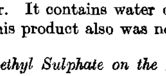
the amount of iodine liberated from potassium iodide in a known weight of substance, only 70 per cent. of the theoretical quantity of chlorine was found to be present.

The sodium salt is prepared by dissolving the chlorine compound in a little warm sodium hydroxide solution. On cooling, the salt crystallises in colourless needles, which may be recrystallised from a little water. It contains water of crystallisation, but analysis showed that this product also was not pure.

Action of Methyl Sulphate on the Hydantoin.

(1) Four grams of the hydantoin were dissolved in sufficient sodium hydroxide to give a clear solution, four grams of methyl sulphate added, and the mixture warmed on the water-bath for an hour. The thick, yellowish precipitate was filtered, washed with dilute hydrochloric acid, then with water, and dried in a vacuum. It crystallised from a mixture of alcohol and water in minute needles, which melted at 307—311°. It was sparingly soluble in water and alcohol, but dissolved readily in alkalis and was reprecipitated unchanged by acids even after boiling with sodium hydroxide solution.

The percentage of nitrogen shows that it contains two methyl groups (Found : N = 12·04, 12·25. $C_{11}H_{10}O_4N_2$ requires N = 11·98 per cent.). The substance is therefore the dimethyl ether of the hydantoin,



(2) Three grams of the hydantoin were dissolved in excess of sodium hydroxide solution (about twice the amount required to dissolve the acid) and 6 grams of methyl sulphate added. On shaking the mixture vigorously it became hot and the layer of methyl sulphate gradually disappeared. The reaction was completed by heating on the water-bath for an hour. A clear solution was then obtained, from which, when cold, a mass of fine, colourless needles gradually separated. They were filtered and recrystallised from hot alcohol.

The substance obtained in this way melts at 137°. It is sparingly soluble in water, very soluble in hot alcohol, and moderately soluble in cold alcohol. It is insoluble in cold solutions of sodium carbonate or hydroxide, but gradually dissolves on heating. The substance is probably the methyl ester of the dimethylated hydantoin described above. In order to confirm this, the substance was prepared in the manner described below.

1-*Methyl 2-Hydrogen 3-Carbamidophthalate.*

1-Methyl 2-hydrogen 3-nitrophthalate is reduced to the amino-compound with stannous chloride and hydrochloric acid as described under aminophthalic acid. The 1-methyl ester of 3-aminophthalic acid is thus obtained in colourless needles, m. p. 150°. The yield is nearly theoretical. Five grams of the amino-ester hydrochloride and 3 grams of potassium *iso*cyanate are dissolved separately in water and the solutions mixed. Sodium carbonate solution is then added until the mixture is only slightly acid. On rubbing the side of the vessel the carbamido-compound begins to separate as a colourless, crystalline powder. After standing overnight, the precipitate is filtered, washed with water, and dried in a vacuum. The yield is 70 per cent. of the theoretical. When heated, the substance melts with decomposition at 162° and resolidifies to a yellow mass, which melts at about 185°.

Methyl Ester of the Hydantoin.

The carbamido-ester is heated on the water-bath with hydrochloric acid as described in the preparation of the free acid (see above). The hydantoin methyl ester is obtained as a colourless powder, which may be recrystallised from dilute alcohol. When heated, it turns yellow at about 180° and melts at 310—312°.

Action of Methyl Sulphate on the Hydantoin Methyl Ester.

Three grams of the ester were mixed with 2·5 grams of methyl sulphate and sufficient sodium hydroxide to give a clear solution on shaking. The mixture gradually became hot, and in order to avoid hydrolysis of the ester it was cooled in water. After a short time the liquid became semi-solid from the separation of the crystalline methyl derivative. The latter was filtered, washed with dilute hydrochloric acid, and dried in a vacuum. The substance melted at 137—140°. It dissolved readily in hot alcohol and after crystallisation melted at 144°. Repeated recrystallisation did not change the melting point. The substance, m. p. 137°, described above is probably identical with this compound, but not quite as pure (Found: N = 11·42. $C_{12}H_{12}O_4N_2$ requires N = 11·29 per cent.). The substance *contains, therefore, three methyl groups*, and is the *methyl* ester of the dimethylated hydantoin,

$$CO_2Me\cdot C_6H_3<\begin{matrix}N{=\!=\!=}C\cdot OMe\\ C(OMe){:}N\end{matrix}.$$

Nitration of the Hydantoin.

Three grams of the hydantoin were dissolved in 25 grams of sulphuric acid by warming gently and 5 grams of fuming nitric acid added. The mixture became hot and acquired a deep red colour; after being heated on the water-bath for an hour, during which the red colour disappeared, the mixture was cooled and poured into 40 c.c. of cold water. The solution, on cooling, deposited a yellow, crystalline precipitate, which was filtered off and dried. It melted at 298° (with decomposition) and, after repeated crystallisation from hot water, at 253°; the melting point was not altered by further crystallisation (Found in material dried at 120°: N = 18·10. $C_9H_5O_6N_3$ *requires* N = 16·73; $C_9H_4O_8N_4$ *requires* N = 18·92 per cent.). The product was therefore a mixture of the mono- and di-nitrohydantoins.

A portion of the crude product (m. p. 298°) was converted into the sodium salt by dissolution in hot sodium carbonate solution. On cooling, the salt crystallised out in glistening yellow plates, which were recrystallised from hot water, and dried at 150° (Found: N = 16·75. $C_9H_4O_6N_3Na$ requires N = 15·38; $C_9H_3O_8N_4Na$ requires N = 17·61 per cent.). Here again the product was a *mixture of the mono- and di-nitro-derivatives.*

Preliminary Note on 4-p-*Hydroxybenzylhydantoin and its Derivatives.*

4-*p*-Hydroxybenzylhydantoin was prepared by Dakin's method (*J. Biol. Chem.*, 1910, **8**, 30). To 6 grams of tyrosine in 30 c.c. of boiling water about 3 grams of potassium *iso*cyanate were added and the liquid boiled until a clear solution was obtained. Twenty c.c. of concentrated hydrochloric acid diluted with 40 c.c. of water were then added and the solution boiled for a quarter of an hour. The hydantoin separated in colourless crystals, which, after cooling, were filtered and washed. The yield was equal to the weight of the original tyrosine.

4-p-*Acetoxybenzylhydantoin.*—Two grams of the hydantoin were mixed with 8 grams of acetic anhydride. No apparent action took place, and the hydantoin remained undissolved until a minute quantity (0·2 gram) of anhydrous sodium acetate was added, when the hydantoin at once passed into solution.* The product was evaporated and water added, when the acetyl derivative separated as a viscous mass, which soon solidified. It was crystallised from

* It is evident that the sodium acetate acts as a catalyst, and it is our intention to study this effect in other cases of acetylation.

dilute alcohol and formed clusters of colourless needles, m. p. 117—118°.

4-p-*Acetoxybenzylhydantoin* OO-*Dimethyl Ether*,

$$OAc\cdot C_6H_4\cdot CH_2\cdot CH<\begin{matrix}C(OMe):N \\ N{=\!=\!=}C\cdot OMe\end{matrix}.$$

—To a mixture of 0·9 gram of the acetyl derivative and 1·5 grams of methyl sulphate a 10 per cent. solution of sodium hydroxide was added drop by drop with gentle warming until the reaction was permanently alkaline. After standing, the oily liquid solidified, and the crystalline mass was filtered, washed, and crystallised from alcohol, when it formed glistening needles, m. p. 144—145° (Found: N = 9·65. $C_{14}H_{16}O_{11}N_2$ requires N = 10·1 per cent.).

4-p-*Hydroxybenzylhydantoin* OO-*Dimethyl Ether*,

$$OH\cdot C_6H_4\cdot CH_2\cdot CH<\begin{matrix}C(OMe):N \\ N{=\!=\!=}C\cdot OMe\end{matrix}.$$

—On boiling the preceding compound with a little concentrated hydrochloric acid it gradually dissolved and glistening foliated crystals were obtained on cooling, which melted at 180—182° after crystallisation from alcohol.

Methyl Ether of the Dimethylated Hydantoin.—One gram of methyl sulphate was added to 0·5 gram of the hydantoin and the mixture made gradually alkaline with sodium hydroxide and warmed until the excess of methyl sulphate was removed. A colourless solid separated, which was filtered, washed with water, and extracted from the unchanged hydantoin with alcohol. After the alcohol had been evaporated and the residue crystallised from toluene, the substance melted at 134° (Found: N = 11·23. $C_{13}H_{16}O_3N_2$ requires N = 11·3 per cent.).

Action of Benzenediazonium Chloride on the Hydantoin.

0·3 Gram of the hydantoin was dissolved in the least quantity of 10 per cent. sodium hydroxide solution. To this solution, diluted to 10 c.c., were added 6 c.c. of a solution containing in 10 c.c. 1 gram of aniline dissolved in 3 c.c. of concentrated hydrochloric acid and 3 c.c. of water and diazotised with 0·8 gram of sodium nitrite. The solntion turned deep red, a brown precipitate formed, and finally a thick, orange, crystalline precipitate separated, which was filtered and washed with cold water. It crystallised from absolute alcohol in clusters of orange needles, which softened at 205°, darkened, owing probably to decomposition, and melted completely at 220° (Found: N = 18·5. $C_{16}H_{13}O_3N_4$ requires N = 18·1 per cent.).

The compound has probably the following formula:

$$NPh{:}N{\cdot}C_6H_3(OH){\cdot}CH_2{\cdot}CH{<}\begin{matrix}CO-NH\\ NH{\cdot}CO\end{matrix}$$

Sodium Salt.—4-*p*-Hydroxybenzylhydantoin dissolves in sodium hydroxide solution, and the sodium salt slowly separates on evaporation or, more rapidly, by addition of alcohol, in colourless, flat, prismatic crystals (Found: Na = 13·6, 13·2, 13·4; H_2O = 26·0. $C_{10}H_8O_3N_2Na_2,5H_2O$ requires Na = 13·5; H_2O = 26·4 per cent.).

For the tyrosine, which served for the above experiments, we are indebted to Dr. H. Raistrick.

THE ORGANIC CHEMICAL LABORATORIES,
THE UNIVERSITY, LEEDS. [*Received, March 18th*, 1921.]

LXXII.—*Organo-derivatives of Thallium. Part I. Some Reactions of Thalliumdialkyl Haloids.*

By ARCHIBALD EDWIN GODDARD.

THE object of the present work was to obtain mixed thallium alkyls of the types TlRR′·Hal. and TlRR′R″. To attain this the alkyls TlR_2·Hal. have first been further investigated and their stability towards various reagents tested.

Meyer and Bertheim (*Ber.*, 1904, **37**, 2051) obtained thalliumdimethyl bromide by the action of magnesium methyl bromide (4 mols.) on thallic chloride (1 mol.) (yield 62·5 per cent. of the theoretical). The general equation given for the reaction was:

$$TlCl_3 + 2MgRCl = TlR_2Cl + 2MgCl_2.$$

The author has found that when 5 molecules of magnesium alkyl haloid to 1 molecule of thallic chloride are used the yield of thalliumdialkyl haloid always approximates to 50 per cent. Only half of the thallium in the thallic chloride of the above equation is thus accounted for, and it is possible that the other half goes to form a trialkyl compound, which may be either a gas, and is evolved during the reaction, or a liquid decomposed by water.

Previous investigators obtained thalliumdimethyl iodide (m. p. 264—266°) by treating the corresponding bromide with potassium iodide, but it is now found that the iodide formed by the use of

magnesium methyl iodide on thallic chloride only shows slight decomposition at 295°.

When the alkaline solution obtained by treating this iodide with moist silver oxide is evaporated in the air, thalliumdimethyl carbonate is formed, and silver chromate and nitrate react with the haloid to yield thalliumdimethyl chromate and nitrate respectively. Copper bronze or metallic sodium in dry solvents has no action on thalliumdialkyl haloids.

In the ethyl series thalliumdiethyl thiocyanate and chromate were obtained by the use of silver salts, but silver dichromate and ferro- and ferri-cyanides failed to give compounds.

Trichloroacetic acid reacts with a solution of thalliumdiethyl hydroxide to give the trichloroacetate.

With the Grignard reagent, thallic chloride gives results analogous to those obtained by Pope and Gibson with auric chloride (T., 1907, **91**, 2061). The resulting thalliumdiethyl bromide, however, whilst reacting easily with silver salts, is quite stable towards bromine when treated under the same conditions as the gold compound; it also failed to react with magnesium phenyl bromide either in the cold or when heated.

Meyer and Bertheim (*loc. cit.*) showed that only spongy thallium was obtained by the interaction of magnesium alkyl haloids and thallous chloride; it is now found that replacement of the latter by the chlorobromide, $Tl_4Cl_3Br_3$, gives the same result (Cushmann, *J. Amer. Chem. Soc.*, 1901, **26**, 505), and that magnesium *iso*propyl iodide and thallic chloride produce thallous iodide in quantitative yield.

In the case of haloids, cyanides, and thiocyanates, in the presence of nitric acid and silver nitrate, the following equation has been found to represent the reaction quantitatively:

$$R_2TlX + AgNO_3 = AgX + R_2TlNO_3,$$

where X = Hal., CN, or SCN. The organic nitrate formed is soluble in water.

EXPERIMENTAL.

Action of Magnesium Methyl Iodide upon Thallic Chloride.

A solution prepared from 7·5 grams of magnesium and 44·4 grams of methyl iodide was added in small amounts with continual shaking to 19·44 grams of thallic chloride dissolved in 75 c.c. of dry ether cooled in a freezing mixture. At first the reaction was very violent and a brownish-red precipitate separated out. When nearly all the Grignard reagent had been added, the colour changed to pale yellow. After remaining at room temperature for half an hour the product was decomposed by dilute hydrochloric acid and

the residue after filtration extracted with boiling dilute ammonia, the solution on cooling depositing shining plates. Yield 8·5 grams (46·2 per cent. of the theoretical). The crude product was purified by boiling with water containing a little potassium iodide, and recrystallising twice from water. The compound thus obtained showed slight decomposition at 295°, but did not melt at 300° (Found: Tl = 56·43; I = 35·20. C_2H_6ITl requires Tl = 56·49; I = 35·15 per cent.).

Thalliumdimethyl iodide is a white solid crystallising in plates, and is moderately soluble in water or ammonia, much less so in alcohol or acetone, and is insoluble in ether or light petroleum.

Preparation of Salts.

The following salts were prepared by boiling an aqueous solution of thalliumdimethyl iodide with silver salts in about 75 c.c. of water and evaporating the solution until crystals appeared. This mode of procedure applies also to the ethyl compounds described, the starting-point in this case being thalliumdiethyl bromide.

Thalliumdimethyl Carbonate.—This was obtained by the interaction of 4·7 grams of the iodide and 4·0 grams of silver oxide, the resulting solution being concentrated in the air. After six crystallisations from alcohol, 2·6 grams of pure product were isolated, the crystals evolving a gas at 255° (Found: Tl = 76·65; CO_3 = 11·38. $C_5H_{12}O_3Tl_2$ requires Tl = 77·22; CO_3 = 11·37 per cent.). The salt crystallises in large hexagonal plates, which are very soluble in water, moderately so in alcohol or acetone, and dissolve slightly in ether. By treatment with mineral acids, carbon dioxide is evolved and salts are formed.

Thalliumdimethyl Chromate.—The crude product obtained from 2 grams of thalliumdimethyl iodide and 1·0 gram of silver chromate, after two recrystallisations from water, gave a theoretical yield of *thalliumdimethyl chromate*, which decomposed at 255° without melting (Found: Tl = 69·74; Cr = 8·75. $C_4H_{12}O_4CrTl_2$ requires Tl = 69·83; Cr = 8·89 per cent.). The salt is a brilliant yellow solid crystallising in plates; it is very soluble in water, alcohol, or acetone, and dissolves slightly in ether or light petroleum.

Thalliumdimethyl Nitrate.—Two grams of thalliumdimethyl iodide and 1·0 gram of silver nitrate gave a crystalline product, which, after two recrystallisations from alcohol, did not melt at 300° (Found: Tl = 68·56. $C_2H_6O_3NTl$ requires Tl = 68·88 per cent.). The *nitrate* crystallises in shining, white plates, and is soluble in water, alcohol, or acetone, but is less soluble in ether.

Attempts to Remove the Iodine from Thalliumdimethyl Iodide.—Two grams of the iodide, 0·5 gram of copper bronze, and 15 c.c. of dry acetone were refluxed on a water-bath for seven hours. The solution was filtered and 1·5 grams of the iodide were recovered unchanged. By treating a similar quantity of the iodide with metallic sodium in dry benzene a like result was obtained. No complex of the type $Me_2Tl{\cdot}TlMe_2$ was isolated in either case.

Thalliumdiethyl Thiocyanate.—By the interaction of 1·0 gram of thalliumdiethyl bromide and 0·8 gram of silver thiocyanate a product was formed, which did not melt at 300° after two recrystallisations from alcohol. Yield 0·6 gram (Found: Tl = 63·49; SCN = 17·64. $C_5H_{10}NSTl$ requires Tl = 63·67; SCN = 18·14 per cent.). The salt forms small, colourless plates, which are readily soluble in water or alcohol, but slightly so in ether.

Thalliumdiethyl Chromate.—The iodide (1·5 grams) and 0·7 gram of silver chromate gave a theoretical yield of *thalliumdiethyl chromate.* After one crystallisation from alcohol, the crystals decomposed with violent explosion at 193° (Found: Tl = 63·35; Cr = 7·87. $C_8H_{20}O_4CrTl_2$ requires Tl = 63·69; Cr = 8·12 per cent.). The salt crystallises in brilliant yellow plates, and is very soluble in water or alcohol, but less so in ether.

Action of Silver Dichromate upon Thalliumdiethyl Bromide.—When 1·36 grams of the bromide and 1·0 gram of the silver salt were used, two crops of crystals (*a*) and (*b*) were obtained. The deposit (*a*) did not melt at 300° and consisted of unchanged bromide (Found: Tl = 59·35. Calc., Tl = 59·61 per cent.). Deposit (*b*) did not depress the melting point of thalliumdiethyl chromate.

Silver Ferro- and Ferri-cyanides and Thalliumdiethyl Bromide.—The usual procedure was adopted, but neither of these silver salts reacted, unchanged bromide being recovered in both cases.

Thalliumdiethyl Trichloroacetate.—The solution obtained from 0·4 gram of thalliumdiethyl bromide and 1·0 gram of silver oxide was acidified with trichloroacetic acid and evaporated, whereby 0·3 gram of crystals was isolated, which did not melt at 300°. When the salt was hydrolysed by potassium hydroxide in the presence of aniline, phenylcarbylamine was formed, the presence of the trichloroacetic acid radicle being thus proved (Found: Tl = 48·01. $C_6H_{10}O_2Cl_3Tl$ requires Tl = 48·03 per cent.). The salt forms white, crystalline plates, and is very soluble in water, alcohol, or acetone, but less so in light petroleum.

Action of Magnesium Ethyl Bromide upon the Compound $Tl_4Cl_3Br_3$.

Five grams of the chlorobromide were added in small quantities to the reagent prepared from 2·0 grams of magnesium and 9·1 grams of ethyl bromide in dry ether. An immediate reaction took place and after decomposition of the solution 3·2 grams of metallic thallium were obtained. As the original chlorobromide contained 3·5 grams of thallium, quantitative reduction had occurred.

Action of Magnesium iso*Propyl Iodide upon Thallic Chloride.*

A solution prepared from 11·75 grams of *iso*propyl iodide and 2·0 grams of magnesium in dry ether was slowly added to a solution of 5·2 grams of thallic chloride in the same solvent, cooled in a freezing mixture. After remaining half an hour the solution was decomposed, but no trace of organic matter was found in the residue. Three grams of thallous iodide were isolated, and as the original thallic chloride should have yielded 3·4 grams, quantitative reduction had occurred.

The author is indebted to the Research Fund of the Chemical Society for a grant which has defrayed the expenses of this investigation.

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[*Received, March 1st*, 1921.]

Mass-spectra and Atomic Weights.

A Lecture Delivered before the Chemical Society on April 7th, 1921.

By Francis William Aston.

Possibly the most important generalisation in the whole history of chemistry is the Atomic Theory put forward by John Dalton in 1803, and it is a striking tribute to the shrewd intuition of that observer that of his five postulates only one seems to be in the least degree faulty, and more than a century of active and unremitting investigation has been necessary to detect the flaw in it.

The postulate in question states that: "Atoms of the same element are similar to one another and equal in weight." Of course, if we take this as a definition of the word "Element" it becomes a truism, but, on the other hand, what Dalton probably meant by an element, and what we understand by the word to-day, is a substance such as hydrogen, oxygen, chlorine, or lead, which has unique chemical properties and cannot be resolved into more elementary constituents by any known chemical process. For many of the well-known elements Dalton's postulate still appears to be strictly true, but for others, probably the majority, it needs some modification.

The general state of opinion at the end of the last century may be gathered from the following quotations from Sir William Ramsay's address to the British Association at Toronto in 1897: "There have been almost innumerable attempts to reduce the differences between atomic weights to regularity by contriving some formula which will express the numbers which represent the weights with all their irregularities. Needless to say, such attempts have in no case been successful. Apparent success is always attained at the expense of accuracy, and the numbers reproduced are not those accepted as the true atomic weights. Such attempts, in my opinion, are futile. Still, the human mind does not rest contented in merely chronicling such an irregularity; it strives to understand why such an irregularity should exist. . . . The idea . . . has been advanced by Professor Schutzenberger, and later by Mr. Crookes, that what we term the atomic weight of an element is a mean; that when we say the atomic weight of oxygen is 16, we merely state that the average atomic weight is 16; and that it is not inconceivable that a certain number of molecules have a weight somewhat higher than 32, while a certain number have a lower weight."

That such conjectures were then regarded as wildly speculative shows how strong was the faith in Dalton's postulate, which is all the more remarkable when we consider that at that time not one single direct experimental proof of it had been offered. Such proof, obviously, can only be obtained by some method which measures the masses of atoms individually, and at that time none had been developed.

The first direct evidence that the atoms of an element were at least approximately equal in mass appears to be that obtained by Sir J. J. Thomson in 1910 by his well-known method of analysis of positive rays. The fact that sharply defined, parabolic streaks were obtained at all proves that the ratio of the masses of the separate particles causing them to the charges of electricity they carry is constant. The latter was known to be a definite unit, e, or a simple multiple of it, so that if the masses of the individual atoms varied amongst each other in an arbitrary manner an indistinct blur would result instead of a clear-cut parabola.

Before going on to the evidence of positive rays in greater detail, it will be as well to consider briefly the evidence upon which was founded the theory of isotopes. The first indication that it might be possible to obtain substances having identical chemical properties but different atomic weights was afforded by the brilliant researches on the radioactive elements made by Sir E. Rutherford and his colleagues. Investigations on the transformations of the different radioactive families showed that certain products, such as lead, could be formed in several ways. Each of the leads so formed was found to have chemical properties identical in every respect with those of ordinary lead, but their method of production precluded any possibility of them all having the same atomic weight. Such bodies, although having different atomic weights, must occupy the same position in the Periodic Table of the elements, and on this account have been called "isotopes" by Professor Soddy.

Moseley's epoch-making discovery has shown us that chemical properties depend, not on atomic weight, but on something much more fundamental, namely, *atomic number*. The atomic number of an element is the number of units of positive electricity on the nucleus of its atoms; the nuclear charge of hydrogen is 1, of helium 2, of lithium 3, and so on. We see, therefore, that isotopes are elements having the same atomic number but different atomic weights.

The theory of isotopes was triumphantly vindicated during the war by the researches of Soddy, Richards, Honigschmidt, and others on the atomic weights of lead found in various radioactive minerals. Quantities were obtained ample for the most

accurate determinations by chemical methods, and the atomic weights were found to differ from each other and from that of ordinary lead by quantities altogether outside possible experimental error.

Long before this convincing proof was forthcoming the theory of isotopes was discussed with the greatest interest in connexion with atomic weights in general. If isotopes occurred among the heavy elements, why should they not be possible among the lighter non-radioactive ones? in which case elements with fractional atomic weights might clearly be mixtures, the constituents having atomic weights equal to whole numbers. This explanation was a very attractive one, for the curious jumble of whole numbers and fractions in the atomic weights, when referred to oxygen as 16, has always been a serious stumbling-block in the way of any simple theory of atom-building. The accurately determined atomic weight of chlorine, 35·46, has certainly nothing to recommend it. It is reminiscent of the number of square yards in a square rod, pole, or perch, but the idea of Nature working on the same lines as the British weights and measures is an eminently unattractive one.

The first support of the isotope theory among non-radioactive elements was given by the anomalous behaviour of the inactive gas neon when analysed by Sir J. J. Thomson's method of positive rays. This peculiarity was that, whereas all elements previously examined gave single, or apparently single, parabolas, that given by neon was definitely double. The brighter curve corresponded roughly with an atomic weight 20, the fainter companion with one of 22, the atomic weight of neon being 20·20. In consequence of reasoning adduced from the characteristics of the line 22, the discoverer was of the opinion that it could not be attributed to any compound, and that therefore it represented a hitherto unknown elementary constituent of neon. This agreed very well with the idea of isotopes which had just been promulgated, so that it was of great importance to investigate the point as fully as possible.

The first line of attack was an attempt at separation by repeated fractionation over charcoal cooled with liquid air, but even after many thousands of operations the result was entirely negative. It is some satisfaction to know that this result was inevitable, as Professor Lindemann has recently shown on thermodynamical grounds. Fractional diffusion through pipeclay was more effective and gave a positive result. An apparent difference of density of 0·7 per cent. between the lightest and heaviest fractions was obtained after an exceedingly laborious set of operations. When the war interrupted the research, it might be said that several independent

lines of reasoning pointed to the idea that neon was a mixture of isotopes, but that none of them could be said to carry the conviction necessary in such an important development.

When the work was recommenced, attention was again directed towards positive rays, for it was clear that if an analysis could be made with such accuracy that it could be demonstrated with certainty that neither of the two atomic weights so determined agreed with the accepted chemical figure, the matter could be regarded as settled. This could not be done with the parabolas already obtained, but the accuracy of measurement was raised to the required degree by means of the arrangement illustrated in

FIG. 1.

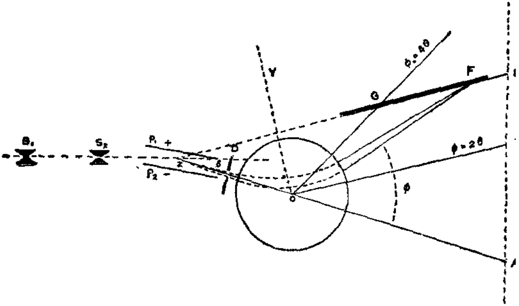
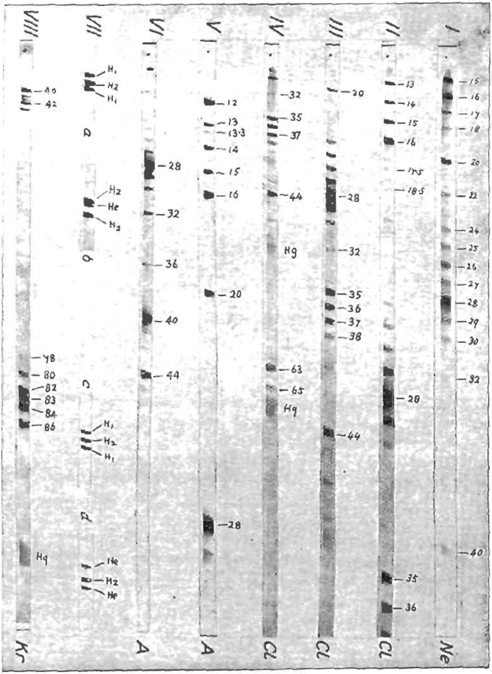


Fig. 1.* Positive rays are sorted out into a thin ribbon by means of the two parallel slits, S_1 S_2, and are then spread into an electric spectrum by means of the charged plates, P_1, P_2. A portion of this spectrum deflected through an angle, θ, is selected by the diaphragm D and passed between the circular poles of a powerful electromagnet, O, the field of which is such as to bend the rays back again through an angle, ϕ, more than twice as great as θ. The result of this is that rays having a constant mass (or more correctly constant m/e) will converge to a focus, F, and that if a photographic plate is placed at GF, as indicated, a *spectrum dependent on mass alone* will be obtained. On account of its analogy to optical apparatus, the instrument has been called a positive ray spectrograph and the spectrum produced a mass-spectrum.

* Reprinted, by permission, from *Phil. Mag.*, 1919, [vi], 38, 710.

FIG. 2.



[To face Trans., p. 631.

Fig. 2 * shows a number of typical mass-spectra obtained by this means. The numbers above the lines indicate the masses they correspond with on the scale O = 16. It will be noticed that the displacement to the right with increasing mass is roughly linear. The measurements of mass made are not absolute, but relative to lines which correspond with known masses. Such lines, due to hydrogen, carbon, oxygen, and their compounds, are generally present as impurities or purposely added, for pure gases are not suitable for the smooth working of the discharge tube. The two principal groups of these reference lines are the C_1 group due to C (12), CH (13), CH_2 (14), CH_3 (15), CH_4, or O (16), and the C_2 group (24 to 30) containing the very strong line C_2H_4 or CO (28). These groups will be seen in several of the spectra reproduced; they give with the CO_2 line (44) a very good scale of reference.

It must be remembered that the ratio of mass to charge is the real quantity measured by the position of the lines. Many of the particles are capable of carrying more than one charge. A particle carrying two charges will appear as having half its real mass, one carrying three charges as if its mass was one-third, and so on. Lines due to these are called lines of the second and the third order. Lines of high order are particularly valuable in extending our scale of reference.

When neon was introduced into the apparatus, four new lines made their appearance at 10, 11, 20, and 22. The first pair are second-order lines and are fainter than the other two. All four are well placed for direct comparison with the standard lines, and a series of consistent measurements showed that to within about one part in a thousand the atomic weights of the isotopes composing neon are 20·00 and 22·00 respectively. Ten per cent. of the latter would bring the mean atomic weight to the accepted value of 20·20 and the relative intensity of the lines agrees well with this proportion. The isotopic constitution of neon seems therefore settled beyond all doubt.

The element chlorine was naturally the next to be analysed, and the explanation of its fractional atomic weight was obvious from the first plate taken. Its mass-spectrum is characterised by four strong first-order lines at 35, 36, 37, 38, with fainter ones at 39, 40. There is no sign whatever of any line at 35·46. The simplest explanation of the group is to suppose the lines 35 and 37 are due to the isotopic chlorines, and lines 36 and 38 to their corresponding hydrochloric acids. The elementary nature of lines 35 and 37 is also indicated by the second-order lines at 17·5, 18·5, and also, when phosgene was used, by the appearance of lines at 63, 65, due to COCl(35) and COCl(37).

* Reprinted, by permission, from *Phil. Mag.*, 1920, [vi], 39.

Quite recently it has been found possible to obtain the spectrum of negatively charged rays. These rays are formed by a normal positively charged ray picking up two electrons. On the negative spectrum of chlorine only two lines, 35 and 37, can be seen, so that the lines at 36 and 38 cannot be due to isotopes of the element. These results, taken with many others which cannot be stated here in detail, show that chlorine is a complex element and that its principal isotopes are of atomic weight 35 and 37. There may be, in addition, a small proportion of a third of weight 39, but this is doubtful. Spectra show the results with chlorine taken with different magnetic field strengths.

The objection has been raised on many occasions that if chlorine consists of isotopes, how is it that its atomic weight has been determined so accurately and so consistently by different chemists? The obvious explanation of this appears to be that all the accurate determinations have been done with chlorine derived originally from the same source, the sea, which has been perfectly mixed for æons. If samples of the element are obtainable from some other original source, it is quite possible that other values of atomic weight will be determined, exactly as in the case of lead.

The mass-spectrum of argon shows an exceedingly bright line at 40, with second-order line at 20 and third-order line at $13\frac{1}{3}$. The last is particularly well placed between known reference lines, and its measurement showed that the triply charged atom causing it had a mass 40·00 very exactly. Now the accepted atomic weight of argon is less than 40, so the presence of a lighter isotope was suggested. This was found at 36 and has now been fully substantiated; its presence to the extent of about 3 per cent. is sufficient to account for the mean atomic weight obtained by density determinations.

The elements hydrogen and helium presented peculiar difficulties, as their lines were too far removed from the reference lines for direct comparison. By means of a special "bracketing" method moderately accurate values were obtained. Helium appears to be exactly 4 on the oxygen scale, but hydrogen is definitely greater than unity; the value obtained agrees very well with that already arrived at by chemical methods, namely, 1·008. At the same time, measurements of the 3 line, first observed by Sir J. J. Thomson, were made, which came out at 3·024, satisfactorily proving it to be due to triatomic hydrogen.

Krypton and xenon gave surprisingly complex results. The former consists of six isotopes 78, 80, 82, 83, 84, 86. The weights of these could be determined with great accuracy by means of the excellent second- and third-order lines they gave. The first experiments with xenon led to the observation of five isotopes; the

provisional values of these were given as one unit too low. Owing to the kindness of Professor Travers and Dr. Masson, I have recently been enabled to repeat the analysis with gas much richer in xenon. With this the second-order lines could be observed and measured. *The five principal isotopes of xenon are 129, 131, 132, 134, 136*; there is apparently a faint sixth component at 128 and a doubtful seventh at 130.

Experiments with boron fluoride indicated that boron has at least two isotopes, 10 and 11, and that fluorine is a simple element of atomic weight 19.

Silicon is another unmistakably complex element having two isotopes, 28 and 29, with a possible additional one, 30.

Bromine was of great interest; as it has an atomic weight almost exactly 80, it might reasonably be expected to be simple and an isobare of one of the kryptons; actually it consists of equal parts of 79 and 81.

Sulphur, *phosphorus, and arsenic are all apparently simple elements. Mercury is certainly mixed, although its closer com*ponents cannot be resolved on the present apparatus. Its very characteristic groups are seen as high as the fifth order, and appear on nearly all the spectra taken. The group consists of a continuous succession of lines forming a band, 197 to 200, a strong line at 202 and a weak one at 204. Recently at Copenhagen Brönsted and Hevesy have succeeded in partly separating the isotopes of mercury by a fractional distillation at extremely low pressure. They give as their figures for the densities compared with that of normal mercury as unity:

Condensed mercury	0·999980
Residual mercury	1·000031

The accuracy claimed is less than one part in a million.

Selenium, tellurium, antimony, and tin have all been used in the discharge tube with no results of any value. This is unfortunate, for the atomic weight of selenium, 79·2, suggests that one of its isotopes must be an isobare of bromine or krypton; also the relation between tellurium and iodine is of great interest.

Iodine, fortunately, gave a very definite result. It is a simple element of atomic weight 127. This is rather surprising, as all the theoretical papers on the isotopic constitution of elements have predicted a complex iodine. Prophecy in physics becomes a difficult trade when experimental results produce these surprises; apparently the only really trustworthy prediction is that there are plenty more in store for us.

The following is a list of elements and isotopes determined by the

mass-spectrograph using the ordinary discharge-tube method for the generation of the rays:

Table of Elements and Isotopes.

Element.	Atomic number.	Atomic weight.	Minimum number of isotopes.	Masses of isotopes in order of intensity.
H	1	1·008	1	1·008
He	2	3·99	1	4
B	5	10·9	2	11, 10
C	6	12·00	1	12
N	7	14·01	1	14
O	8	16·00	1	16
F	9	19·00	1	19
Ne	10	20·20	2	20, 22, (21)
Si	14	28·3	2	28, 29, (30)
P	15	31·04	1	31
S.........	16	32·06	1	32
Cl	17	35·46	2	35, 37, (39)
A	18	39·88	(2)	40, (36)
As	33	74·96	1	75
Br	35	79·92	2	79, 81
Kr	36	82·92	6	84, 86, 82, 83, 80, 78
I	53	126·92	1	127
X	54	130·2	5, (7)	129, 132, 131, 134, 136, (128, 130?)
Hg	80	200·6	(6)	(197–200), 202, 204

(Numbers in brackets are provisional only.)

By using a heated anode coated with metallic salts it has recently been found possible to obtain the mass-spectra of the elements of the lithium group. Lithium proves to be a mixture of isotopes 6 and 7.

Sodium is simple, as its atomic weight, 23·00, would lead us to expect; it forms a convenient standard of mass, as oxygen and the other non-metallic elements do not appear when this method is employed.

Potassium gives a strong line at 39 and a very weak one at 41. Rubidium gives a pair of much more equal intensity at 85 and 87. The relative intensities of these two lines correspond satisfactorily with the accepted atomic weight. Although the atomic weight of cæsium (132·81) indicates complexity, no line except one at 133 has so far been distinguished. If a lighter isotope exists, its proportion must be very small.

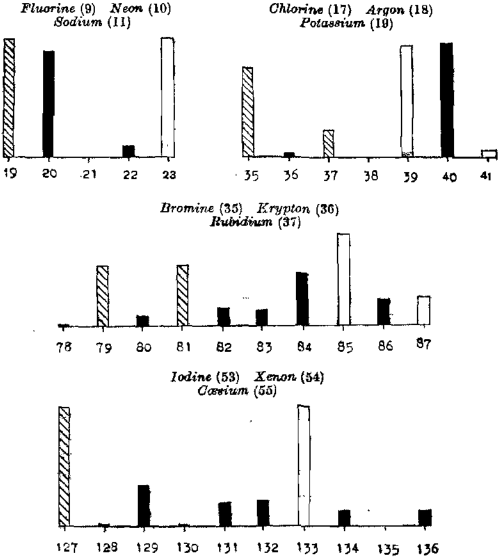
The relation between the halogens, the inactive gases and the alkali metals is indicated in Fig. 3. The heights of the columns above the atomic weights roughly represent the proportions of the isotopes present. It will be noted that, with one very doubtful exception, Cl (39), there are no isobares; and also that there is a very marked tendency for even atomic numbers to be associated with even atomic weights and odd with odd.

It is clear that the *order* of the chemical or "mean" atomic weights in the Periodic Table has no practical significance; anomalous cases such as argon and potassium are simply due to the relative proportions of their heavier and lighter isotopes.

By far the most important result of these measurements is that,

Fig. 3.

Isotopes of the Halogens, the Inactive Gases, and the Alkali Metals.



with the exception of hydrogen, the weights of the atoms of all the elements measured, and therefore almost certainly of all elements, are whole numbers to the accuracy of experiment, in most cases about one part in a thousand. Of course, the error expressed in fractions of a unit increases with the weight measured, but with the lighter elements the divergence from the whole-number rule is extremely small.

This enables the most sweeping simplifications to be made in our ideas of mass. The original hypothesis of Prout put forward in 1815, that all atoms were themselves built of atoms of protyle, a hypothetical element which he tried to identify with hydrogen, is now re-established, with the modification that the primordial atoms are of two kinds : atoms of positive and of negative electricity.

Although the latter unit has long been known to us as an "electron," its mate, which appears to be the real unit of mass, has only recently been given the name of "proton."

The Rutherford atom, whether we take Bohr's or Langmuir's development of it, consists essentially of a positively charged central nucleus around which are set planetary electrons at distances great compared with the dimensions of the nucleus itself.

As has been stated, the chemical properties of an element depend solely on its atomic number, which is the charge on its nucleus expressed in terms of the unit charge, e. A neutral atom of an element of atomic number N has a nucleus consisting of $K + N$ protons and K electrons, and around this nucleus are set N electrons. The weight of an electron on the scale we are using is 0·0005, so that it may be neglected. The weight of this atom will therefore be $K + N$, so that if no restrictions are placed on the value of K any number of isotopes are possible.

The first restriction is that, excepting in the case of hydrogen, K can never be less than N, for the atomic weight of an element is always found equal to or greater than twice its atomic number. The upper values of K also seem to be limited, for, so far, no two isotopes of the same element have been found differing by more than 10 per cent. of its mean atomic weight; the greatest numerical difference is eight units in the case of krypton. Except for the remarkable fact that in the great majority of cases so far determined K is an even number, the actual occurrence of isotopes does not seem to follow any law at present obvious, although their number is probably limited by some condition of stability.

Protons and electrons may therefore be regarded as the bricks out of which atoms have been constructed. An atom of atomic weight m is turned into one of atomic weight $m + 1$ by the addition of a proton plus an electron. If both enter the nucleus, the new element will be an isotope of the old one, for the nuclear charge has not been altered. On the other hand, if the proton alone enters the nucleus and the electron remains outside, an element of next higher atomic number will be formed. If both these new configurations are possible, they will represent elements of the same atomic weight but with different chemical properties. Such

elements are called "isobares" and are actually known among the radioactive elements.

The case of the element hydrogen is unique; its atom appears to consist of a single proton as nucleus with one planetary electron. It is the only atom in which the nucleus is not composed of a number of protons packed exceedingly closely together. Theory indicates that when such close packing takes place the effective mass will be reduced, so that when four protons are packed together with two electrons to form the helium nucleus this will have a weight rather less than four times that of the hydrogen nucleus, which is actually the case.

It is not to be supposed that the whole-number rule is of exact mathematical accuracy, for the unit of the oxygen scale is a "packed" proton and its value is sure to alter slightly with the degree of packing. On this account it is of the greatest importance to push the accuracy of methods of atomic weighing as far as possible, for variations from the whole-number rule, if they could be determined with precision, would give us some hope of laying bare that innermost of secrets, the actual configuration of the charges in the nucleus.

The results I have brought before you this evening lie on the border line of physics and chemistry, and although as a chemist I view with some dismay the possibility of eighteen different mercuric chlorides, as a physicist it is a great relief to find that Nature employs at least approximately standard bricks in her operations of element building.

LXXIII.—*Organic Derivatives of Tellurium. Part IV. Action of Ammonia and the Alkalis upon α-Dimethyltelluronium Di-iodide.*

By (the late) RICHARD HENRY VERNON.

Action of Ammonia.—When dry ammonia is led over the α-iodide (T., 1920, **117**, 90) the bright red salt rapidly becomes decolorised, and is transformed by continued action into a milky, semi-fluid mass. The composition at this stage corresponds with the formula $TeMe_2I_2,6NH_3$ and there is no further absorption.

A whole series of very unstable compounds of the type

$$TeMe_2I_2,nNH_3,$$

where $n = 1 \ldots 6$, exists. As n increases, the red colour of the iodide gradually disappears, and for $n = 3$ vanishes completely,

$TeMe_2I_2,3NH_3$ having the appearance of white porcelain. From $n = 3$ onwards, the solid becomes more and more liquid, and is nearly fluid when $n = 6$. Moreover, as the ammonia can be entirely removed, leaving the unaltered iodide, the system is reversible and can be expressed by the equation

$$TeMe_2I_2,nNH_3 \rightleftharpoons TeMe_2I_2 + nNH_3.$$

The stability of the derivatives is approximately inversely proportional to n; the compound corresponding with $n = 2$ loses its ammonia but slowly. A paper impregnated with a chloroform solution of the iodide is about as sensitive to ammonia as litmus, the discoloured paper becoming red again after a short interval.

The action of an aqueous solution of ammonia upon the α-iodide is totally different from that of the dry gas, and is very much more complicated.

Di-iodotetramethylditelluronium Oxide.—When the iodide is treated with an excess of ammonium hydroxide on the water-bath, a film of bright yellow oil gradually forms on the surface of the more or less coloured solution. On cooling, this film partly solidifies and changes rather suddenly, especially on trituration with a glass rod, to a nearly colourless, very heavy, crystalline powder. The melting point fluctuates between 112° and 125°, and repeated analyses have shown considerable variations in both carbon and hydrogen.

The nature of this substance, however, could be definitely established, because from the solution in boiling chloroform were deposited overnight deep golden yellow cubic crystals of *di-iodotetramethylditelluronium oxide* containing half a molecule of chloroform o[f] crystallisation, $O(TeMe_2I)_2,\frac{1}{2}CHCl_3$ (hereinafter termed the oxy iodide). The constitution follows from that of the α-iodide, an[d] cannot be of the form *$TeMe_2O,TeMe_2I_2,\frac{1}{2}CHCl_3$, since this woul[d] be a β- and not an α-derivative.

Hydrolysis of the Oxyiodide.—By the action of boiling wate[r] the chloroform is removed and the molecule split up into th[e] α-iodide and the α-base.

$$O(TeMe_2I)_2 + H_2O \rightarrow 2TeMe_2I{\cdot}OH \rightarrow TeMe_2I_2 + TeMe_2(OH)_2.$$

The condensation of the iodide and the base regenerates the ox[y]iodide. It is immaterial whether aqueous ammonia or the α-base (T[.,] 1920, **117**, 92) is allowed to act upon the iodide; in both cases th[e] oxyiodide is obtained.

The presumption that the alkali hydroxides and carbonat[es] would react in a similar manner was fully confirmed; moreove[r] it was found that 1 mol. of the iodide reacted with 1 mol. of th[e]

* The β-base has the constitution $TeMe_2O$ (T., 1920, **117**, 889).

alkali or with a $\frac{1}{2}$ mol. of the carbonate. The results so far achieved can be expressed by three types of equations.

$$\begin{aligned}
&(1)\ TeMe_2I_2 + TeMe_2(OH)_2 \rightarrow 2TeMe_2I{\cdot}OH \longrightarrow TeMe_2{<}^{I}_{O} \\
&(2)\ 2TeMe_2I_2 + 2MOH \rightarrow 2MI + 2TeMe_2I{\cdot}OH \longrightarrow TeMe_2{<}^{I}_{O} \\
&(3)\ 2TeMe_2I_2 + K_2CO_3 \rightarrow 2KI + (TeMe_2I{\cdot}O)_2CO \longrightarrow TeMe_2{<}_{I}
\end{aligned}$$

in which M represents any of the alkali metals or the ammonium radicle.

Evidently the action of alkali hydroxides and carbonates upon the iodide is partly to convert it into the α-base, which in its turn reacts with the unaltered iodide to give the oxyiodide. The whole investigation therefore centres on the interaction between the α-base and its own iodide.

Heeren (*Jahresbericht über die Fortschritte der Chemie*, 1861, 566) investigated the action of ammonia upon what were evidently the α-chloride and α-bromide, and expressed his results by the formula ($C_2H_3TeO + C_2H_3TeX$), where X is either chlorine or bromine. These were evidently the chloro- and bromo-analogues of the oxyiodide. As the author mentions no difficulty in connexion with the preparation and study of the " Oxychlorür " and " Oxybromür," they must be moderately stable, and possibly soluble in water without that complete hydrolysis so characteristic of the corresponding iodide.

Wöhler and Dean (*Annalen*, 1855, **93**, 236) also mention that ammonia and the α-chloride react to produce " Tellurmethyl-Oxychlorür " [$C_2H_3TeCl + C_2H_3TeO$].

Di-iodohexamethyltritelluronium Dioxide.—The yellow oil (an unstable form of the oxyiodide) produced when an aqueous solution of ammonia interacted with the iodide eventually disappeared on the continued addition of ammonia and the colourless solution deposited glistening, white scales on cooling.

The same result was produced when the ammonia was replaced by the α-base, and provided that at least two molecules of the base were present to one of the iodide, a copious precipitate of the scales was invariably obtained. The substance, m. p. 152°, proved to be *di-iodohexamethyltritelluronium dioxide*,

$$TeMe_2I{\cdot}O{\cdot}TeMe_2{\cdot}O{\cdot}TeMe_2I.$$

It follows, therefore, that the base and the iodide react in two different ways, the course being determined by the quantity of the base present.

$$\text{I. } TeMe_2(OH)_2 + TeMe_2I_2 = Te_2Me_4I_2O + H_2O.$$

$$\text{II. } 2TeMe_2(OH)_2 + TeMe_2I_2 = Te_3Me_6I_2O_2 + 2H_2O.$$

In these reactions the base can be replaced by any hydroxide or carbonate. In regard to equation II, it is immaterial how much

base is present, the reaction does not extend beyond the dioxyiodide, and a longer chain has never been obtained.

Hydrolysis of the Dioxyiodide.—This hydrolysis is similar to that of the oxyiodide. When a large excess of water is used the base and the iodide are produced,

$$Te_3Me_6I_2O_2 + 2H_2O = TeMe_2I_2 + 2TeMe_2(OH)_2;$$

when, on the other hand, insufficient hydrolysis occurs, the oxyiodide and the base are obtained,

$$Te_3Me_6I_2O_2 + H_2O = Te_2Me_4I_2O + TeMe_2(OH)_2.$$

The latter reaction is the most suitable method of preparing the crystalline oxyiodide.

The Possibility of the Existence of an Isomeric Oxyiodide.—In view of the existence of the two series of isomeric dimethyltelluronium dihaloid salts, it was thought that two isomeric oxyiodides might exist, the β-oxyiodide resulting from the β-base and the β-iodide. Since, however, trimethyltelluronium iodide is formed when an alkali carbonate reacts with the β-iodide (T., 1920, **117**, 895) and further investigation has shown that the same compound is produced when either the β-base or sodium hydroxide reacts with the β-iodide, the existence of the β-oxyiodide is improbable all attempts to prepare it have given negative results.

EXPERIMENTAL.

Action of Ammonia upon α-Dimethyltelluronium Di-iodide.

If dry ammonia is passed over the iodide contained in a weighe boat the amount of gas absorbed can be readily estimated. Satu ation will take place in about two and a half hours, the whit semi-fluid substance then having the composition $TeMe_2I_2,6NH$ When dry air is led over this substance, partial dissociation int the iodide and ammonia occurs. After forty-eight hours fo molecules of ammonia will have been removed and the coloure relatively stable substance, $TeMe_2I_2,2NH_3$, will remain. Even th will eventually lose its ammonia, and complete dissociation into t iodide and ammonia will have occurred after several days.

Di-iodohexamethyltritelluronium Dioxide, $TeMe_2(O{\cdot}TeMe_2I)_2$.

The dioxyiodide can be prepared by the action of an excess any alkali hydroxide or carbonate or of an aqueous solution ammonia upon the α-iodide. The product, however, is a mixt of the anhydrous (scales) and the hydrated (plates) dioxyiodid and since the latter is hydrolysed to the oxyiodide by its o water of crystallisation, a pure preparation of the dioxyiod cannot be obtained.

The following method gave excellent results. A solution of the α-base prepared from 24 grams of the α-iodide (T., 1920, **117**, 92) was diluted to 150 c.c. and boiled with 6 grams * of the powdered α-iodide. The latter rapidly disappeared and the solution became colourless. It was evaporated to about one-third of its bulk (the slightest tinge of yellow indicates an excess of iodide) and suddenly cooled, and the glistening scales that separated were collected, washed with absolute alcohol, and dried over calcium chloride; yield 4—6 grams.

Di-iodohexamethyltritelluronium dioxide crystallises in minute, colourless, anhydrous scales, melts and decomposes at 152°, and is insoluble in all solvents except water, by which it is extensively hydrolysed. The substance becomes bright red by contact with acids or acid vapour, yields its iodine quantitatively to silver nitrate and is converted into the α-base by silver oxide (Found: C = 9·46, 9·43; H = 2·48, 2·37; I = 33·29, 33·33; M [by the cryoscopic method in water] = 163, 170. $C_6H_{18}O_2I_2Te_3$ requires C = 9·49; H = 2·37; I = 33·48 per cent. M = 758).

The hydrated dioxyiodide, m. p. about 145°, crystallises in large, transparent, highly refrangent, hexagonal plates with bevelled edges. These are sometimes 1 mm. thick, as much as 10 mm. in diameter, and contain ½ molecule of water; this quantity, however, does not appear to be absolutely constant (Found: I = 33·19; H_2O = 1·00. $C_6H_{18}O_2I_2Te_3,\frac{1}{2}H_2O$ requires I = 33·09; H_2O = 1·17 per cent.). When the plates are dehydrated over phosphoric oxide the melting point rises to 152° (m. p. of the anhydrous dioxyiodide). Scales of the anhydrous dioxyiodide separate from a solution of the plates in a minimum quantity of concentrated ammonia.

The plates retain their transparency and remain unaltered so long as they are covered by the liquor from which they were precipitated. When dried in the air, however, they rapidly lose their transparency, and become yellow and sometimes red, owing to hydrolysis by the water of crystallisation.

Di-iodotetramethylditelluronium Oxide, $O(TeMe_2I)_2$.

The oxyiodide is best prepared by crystallisation of the crude product obtained by the hydrolysis of the dioxyiodide.

Preparation of the Crude Oxyiodide.—(*A*).—The pure dioxyiodide (3 grams) was boiled for a few minutes with 30 c.c. of water, the clear yellow solution cooled, and crystallisation of the viscous,

* With this quantity the base was present in considerable excess. The best proportion is 2½—4 molecules of the base to 1 molecule of the iodide.

ellow precipitate, which took place suddenly with loss of colour, promoted by friction. The powder was collected and dried over calcium chloride, and it then melted at about 120°; the yield was about 75 per cent. of the weight of the dioxyiodide.

(*B*).—Since the hydrolysis of a mixture of the hydrated and anhydrous dioxyiodide necessarily gives the oxyiodide, the following, simpler ammonia process can be used to prepare the dioxyiodide, whereby the somewhat lengthy and expensive preparation of the α-base is avoided.

A concentrated solution of ammonia was added slowly to α-dimethyltelluronium di-iodide (about 2 c.c. to 1 gram), which was almost instantly decolorised and caked to a hard, white mass, more or less discoloured by metallic tellurium. This was brought into solution by grinding and by the careful addition of a few drops of water. The clear, colourless, filtered solution, from which the excess of ammonia had been removed in a vacuum, deposited after a few hours both plates and scales in varying proportions, the plates, which were sometimes quite large, generally coming down first. The precipitate was filtered and dried and then melted at 140—147°.

These yellow crystals of crude dioxyiodide were treated by method (*A*), the yield of crude oxyiodide being about one-third of the weight of the iodide taken.

Preparation of the Pure (Crystallised) Oxyiodide.—Each gram of the crude oxyiodide prepared according to (*A*) or (*B*) is dissolved in 7—8 c.c. of water, and the mixture just brought to the boil. The clear yellow solution must be immediately filtered through a really hot funnel and should at once begin to crystallise. A yellow, oily film was at times noticed on the surface of the liquid, and its crystallisation observed. If the solution is too concentrated, only a portion of the oil will crystallise, and the remainder will solidify as a bright yellow powder, and a mixture of scales and yellow powder will invariably result. Repeated attempts have been made to rectify (addition of base, concentration, dilution, etc.) solutions like the above, but nothing can be done with them, and the whole preparation must be started afresh.

In a successful experiment, the mother liquor becomes perfectly colourless, and deposits scales of the pure oxide. These are filtered washed with alcohol, and dried over calcium chloride. The yield i about one-half the weight of the crude oxide used.

Di-iodotetramethylditelluronium oxide, which melts and decom poses at 115°, crystallises in anhydrous, greenish-yellow scale sometimes 1 or 2 mm. in diameter. It is quite stable at the ordinar temperature and is insoluble in all solvents with the exception water and chloroform, being extensively hydrolysed by the form

solvent. It behaves like the dioxyiodide towards acids, silver nitrate, and silver oxide, and exists in another modification, as a bright yellow, unstable oil (Found: C = 8·34, 8·07; H = 2·15, 2·09; I = 43·30; M [by the cryoscopic method in water] = 143. $C_4H_{12}OI_2Te_2$ requires C = 8·20; H = 2·05; I = 43·41 per cent. M = 585).

Preparation of the Oxyiodide containing Chloroform of Crystallisation.—It suffices to dissolve the pure oxide in boiling chloroform and allow to crystallise. Since the pure oxide is very difficult to prepare, the following method is more convenient.

A few grams of the thoroughly dried crude oxyiodide are boiled with 50 c.c. of chloroform until the solvent becomes deep golden-yellow. The solution is filtered and the extraction process repeated with the residue. On the next day the extracts will have deposited crystals, which are washed with chloroform, in which they are quite insoluble, and dried over calcium chloride. The yield is somewhat less than the weight of crude oxide taken. The substance forms pure golden-yellow, cubic crystals of remarkable beauty, which exhibit an extraordinary power of refraction, the bottom of a beaker covered with them producing a kaleidoscopic effect. The crystals are not stable, and after twenty-four hours or so will have become opaque and disintegrated into a yellow powder. The substance melts and decomposes at about 116°, and is insoluble in all solvents, including chloroform, except on very prolonged boiling (Found: C = 8·36; H = 1·91; I = 39·29. $2Te_2Me_4I_2O,CHCl_3$ requires C = 8·37; H = 1·93; I = 39·39 per cent.).

Action of Alkali Hydroxides upon the α-Iodide.

When the α-iodide, dissolved in alcohol, is titrated with 0·1*N*-sodium hydroxide, decolorisation follows on the addition of 1 mol. of the alkali to 1 mol. of the iodide (Found: NaOH = 10·87 grams per 100 grams of the iodide. Calc., NaOH = 9·73 grams).

The behaviour is similar towards the alkali carbonates, but in this case 2 mols. of the iodide require one of the carbonate (Found: Na_2CO_3 = 11·5 grams. Calc., Na_2CO_3 = 12·9 grams).

That the action of alkali hydroxide or carbonate upon the iodide is similar to the action of the base or of ammonia is shown when the iodide (1 mol.) is boiled with 0·1*N*-sodium hydroxide (1 mol.); the usual yellow oil results, with subsequent production of the crude oxyiodide (Found: C = 8·41; H = 1·83; I = 43·21 per cent.).

Since Part I of the present paper was published, several further observations relative to the dihaloids have been made. These are now appended.

Preparation of the α-Dihaloids.—A simple method of obtaining the α-chloride and the α-bromide consists in boiling the α-iodide for a few minutes with an excess of nitric acid (one part) and water (one part). After cooling, the iodine is decanted or filtered off, and the solution, which is coloured by iodine, evaporated on the water-bath, when it becomes colourless and ultimately deposits crystals of the α-nitrate. The excess of acid is driven off, and the nitrate dissolved in water and treated with concentrated hydrochloric or hydrobromic acid. One crystallisation of the product from ethyl alcohol containing a trace of the corresponding acid will give the pure salt.

Purification of the β-Dihaloids.—A very remarkable distinction between the α- and the β-dihaloids is that the α-series is very soluble in chloroform, whereas the β-series is not, and to such an extent is this the case that the β-dihaloids can be precipitated quantitatively from solutions by the addition of chloroform. Moreover, the precipitates obtained in this way are beautifully crystalline. Both α- and β-dihaloids are, however, very soluble in acetone, but do not crystallise well from it.

These properties are especially useful in the case of the β-iodide, where the crystallisation of the crude iodide from methyl alcohol, etc., involves considerable loss.

A solution of the crude β-iodide (T., 1920, **117**, 95), a purple powder, in a *minimum* quantity of acetone is filtered (there is little, if any, residue) and allowed to cool; by the gradual addition of chloroform beautiful, green, iridescent scales of the β-iodide are deposited in nearly quantitative yield.

The *α-dinitrate*, $TeMe_2(NO_3)_2$, is prepared by the action of nitric acid upon dimethyltelluride or upon the α-iodide. After one crystallisation from water the pure white salt melts sharply at 142°.

The erroneous formula, $TeMe_2O,HNO_3$, ascribed to this nitrate by Wöhler and Dean (*loc. cit.*) has been repeated in the text-books by Meyer and Jacobson ("Organische Chemie," Vol. I, 336 [1907]) and Beilstein ("Organische Chemie," Vol. I, 292 [1918]). Richter ("Lexikon," Vol. I, 148 [1915]) gives $TeMe_2(NO_3)_2$. The constitution $TeMe_2O,2HNO_3$ is also frequently quoted.

Analysis of the nitrate obtained from methyl telluride and nitric acid by Wöhler and Dean's method is alone sufficient to show that the formula $TeMe_2O,HNO_3$ must be incorrect, because two NO_3-groups enter the molecule. The analytical results would agree far more closely with the formula $TeMe_2O,2HNO_3$, but quite apart from analysis this is also out of the question, since it is the formula of a β-derivative, not of an α-derivative.

Again, since: α-iodide $\overset{HNO_3}{\rightleftharpoons}$ α-nitrate, the constitution of the

nitrate must be similar to that of the α-iodide, namely, $\frac{Me}{NO_3}>Te<\frac{NO_3}{Me}$ (compare T., 1920, **117**, 889).

This is also substantiated by analysis [Found : C = 8·69; H = 2·21; N = 9·96. $TeMe_2(NO_3)_2$ requires C = 8·53; H = 2·13; N = 9·78 per cent.]. The α-nitrate is somewhat explosive, and is difficult to combust.

The β-*Dinitrate*, $TeMe_2(NO_3)_2$.—From a solution of the β-base in concentrated nitric acid, fibrous, colourless crystals will be slowly deposited. These are so soluble in water that they cannot be crystallised from it, the solution yielding a solid, glassy mass when kept over phosphoric oxide.

The analysis of the substance showed abnormal results, the percentage of carbon being 1·5 too low, and the tendency of the methyl groups to wander, noted in the case of the β-dihaloids (T., 1920, **117**, 891), was again observed here. That these still occupy the *cis*-position is proved by the formation of the β-iodide by the action of hydriodic acid. This in its turn regenerates the β-base by treatment with silver oxide.

Action of Iodine upon the α-Iodide.—Scott (P., 1904, **20**, 157) has already mentioned the formation of a di-iodide of trimethyltelluronium iodide, $TeMe_3I_3$. It has now been observed that from a solution of molecular quantities of the α-iodide and iodine in ethyl acetate the *di-iodide* of the α-iodide is deposited in large, bluish-black crystals, which are not very stable and give off traces of iodine (Found: I = 75·55. $TeMe_2I_4$ requires I = 76·33 per cent.).

As two atoms of iodine can be removed from this compound, leaving the unaltered α-iodide, the constitution is probably $[TeMe_2I_2]I_2$, and the molecule does not contain sexavalent tellurium. The β-iodide, in contrast to the α-, does not react with iodine.

This paper is the last of the present series on "Organic Derivatives of Tellurium." There is still much work to be done on this subject, and it would be of interest to find out whether other aliphatic derivatives, such as diethyltelluronium di-iodide,* also exist in two isomeric forms.

* The usual method (Wöhler, *Annalen*, 1840, **35**, 111; 1852, **84**, 79; Mallet, *ibid.*, 1851, **79**, 223) of preparing diethyltelluronium di-iodide is by oxidation of ethyl telluride with nitric acid and subsequent action of hydriodic acid upon the nitrate.

It has been found that the substance (yield about 40 per cent.) can be obtained when equivalent quantities of ethyl iodide and tellurium are heated at 100° in a sealed tube for a fortnight. There is no evidence of pressure when the cold tube is opened. The salt can be extracted with absolute alcohol, and from the solution large, reddish-brown crystals, m. p. 57°, are

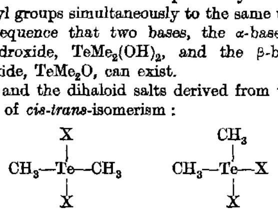
The reason that no further investigation is being undertaken is entirely due to the intolerable * nature of tellurium and its derivatives.

Summary of Results.

(1) Six dimethyltelluronium dihaloids, $TeMe_2X_2$, exist in two isomeric series, each containing three members.

(2) This duplication is due to the possibility of the attachment of two hydroxyl groups simultaneously to the same tellurium atom, with the consequence that two bases, the α-base, dimethyltelluronium dihydroxide, $TeMe_2(OH)_2$, and the β-base, dimethyltelluronium oxide, $TeMe_2O$, can exist.

These bases and the dihaloid salts derived from them are probably instances of *cis-trans*-isomerism:



α- or *trans*-form. β- or *cis*-form.

where X = OH or a halogen atom.

(3) The *trans*-dihaloids have a normal constitution, as is evident from their perfectly normal behaviour. The *cis*-dihaloids behave quite differently, the molecule appearing to be in a state of strain. This condition is evidently brought about by the hydroxyl groups in the *trans*- (normal) position becoming distorted during the transition from the α- to the β-base; in other words, two valencies which are normally widely separated become forced into coincidence.

(4) The crystallographic, pharmacological, and chemical behaviour of these dihaloids, and their absorption spectra, have been compared.

The author's thanks are due to the Committee of Scientific and Industrial Research for a grant which was invaluable during that

obtained (Found: C = 11·13; H = 2·3. $C_4H_{10}I_2Te$ requires C = 10·93; H = 2·27 per cent.).

The base results by the action of silver oxide upon the iodide. The aqueous solution has the usual basic properties and gives the corresponding haloids by treatment with halogen acids. It appears to deposit tellurium on prolonged keeping.

If this base does not decompose when its solution is evaporated to dryness, but gives diethyltelluronium oxide, the existence of two haloid series would be highly probable.

Dibenzyltelluronium di-iodide also can be prepared by the action of benzyl iodide upon tellurium at 100° in a sealed tube. It forms dark brown or orange crystals, m. p. 134°.

* It is indeed remarkable that a substance can permeate the body to the extent that tellurium does without producing dangerous effects.

difficult period of transition from military to civilian life, to Sir Wm. Pope (at whose suggestion this work was originally undertaken), to Mr. W. H. Mills for his unfailing interest, help, and advice, and to Mr. Fred Flack for much assistance with the analyses.

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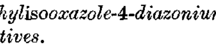
CAMBRIDGE. [*Received, March* 14*th*, 1921.]

LXXIV.—*Non-aromatic Diazonium Salts. Part VI. 3 : 5-Dimethylisooxazole-4-diazonium Salts and their Azo-derivatives.*

By GILBERT T. MORGAN and HENRY BURGESS.

IT has become increasingly evident in recent years that the property of diazotisability is not confined to the amines of the aromatic series, inasmuch as other primary bases belonging to several heterocyclic systems have manifested this property in varying degrees. The existence of a six-membered ring is certainly not essential to diazotisability, because various amines of the five-membered triazole, thiazole, pyrazole, and pyrazolone series are capable of furnishing diazonium salts. These rings are, however, unsaturated, and in all probability this condition is essential to the production of true diazonium compounds. Diazotisable amines contain the group $H_2N\cdot C\lessgtr$ and have, in addition, other foci of unsaturation. In the aromatic series, the residual affinity is furnished by the unsaturated benzenoid group,



The six latent valencies of the aromatic nucleus may possibly saturate the residual affinity of the diazonium radicle, which on the basis of quinquevalent nitrogen, also possesses six integral valencies.

4-Amino-3 : 5-dimethylpyrazole is a diacidic base, but the corresponding diazonium hydroxide functions as a strong monoacidic base, giving rise to remarkably stable diazonium salts

$$H_2N\cdot C\begin{cases}CMe{:}N\\ CMe\cdot NH\end{cases} \qquad HO\cdot N_2\cdot C\begin{cases}CMe{:}N\\ CMe\cdot NH\end{cases}$$

in which the salt-forming properties of the imino-group have become merged into those of the diazonium radicle (Morgan and Reilly, T., 1914, **105**, 435).

The close analogy which exists between the imino-group and oxidic oxygen renders interesting a comparison of the compounds of the *iso*oxazole series with those of the pyrazole group, and the results obtained by a study of the former series are recorded below.

Substitution products of the *iso*oxazole series have not hitherto been described. 3 : 5-Dimethyl*iso*oxazole, the condensation product of acetylacetone and hydroxylamine, undergoes nitration in nitric–sulphuric acid to yield 4-*nitro*-3 : 5-*dimethyl*iso*oxazole*, a well-defined, crystalline substance to which the following constitution (I) may be ascribed

$$NO_2\cdot C{<}\begin{matrix}CMe{:}N\\ CMe\cdot O\end{matrix} \qquad\qquad H_2N\cdot C{<}\begin{matrix}CMe{:}N\\ CMe\cdot O\end{matrix}$$

(I.) (II.)

The reduction of this nitro-compound, a matter of some experimental difficulty, was finally accomplished by the use of amalgamated aluminium and moist ether.

4-*Amino*-3 : 5-*dimethyl*iso*oxazole* (II), a colourless, crystalline, mono-acidic base, yields characteristic azomethine condensation products (Schiff bases) with the aromatic aldehydes. Its soluble salts with the mineral acids are readily diazotisable in aqueous solutions. The crystalline and sparingly soluble 3 : 5-*dimethyl*iso*oxazole*-4-*diazonium aurichloride* (III),

$$\begin{matrix}N{:}CMe\\ O\cdot CMe\end{matrix}{>}C\cdot N_2\cdot AuCl_4,$$

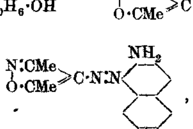
(III.)

has the normal constitution and retains its coupling powers unchanged for an indefinite time. The diazonium chloride, which is very soluble, decomposes at the ordinary temperature and more rapidly on warming; it is far less stable than the corresponding diazonium salt from 4-amino-3 : 5-dimethylpyrazole.

The foregoing diazonium salts couple readily with β-naphthol in alkaline solution, resorcinol in aqueous solution, or with β-naphthylamine dissolved in glacial acetic acid, yielding well-defined coloured, crystalline azo-derivatives,

$$\begin{matrix}N{:}CMe\\ O\cdot CMe\end{matrix}{>}C\cdot N{:}N\cdot C_{10}H_6\cdot OH \qquad\qquad \begin{matrix}N{:}CMe\\ O\cdot CMe\end{matrix}{>}C\cdot N{:}N\cdot C_6H_3(OH)_2$$

(IV.) (V.)



(VI.)

giving characteristic colorations with concentrated sulphuric acid

EXPERIMENTAL.

3 : 5-Dimethyl*iso*oxazole, the starting-point in this research, was prepared by a modification of Combes's method for obtaining the monoxime of acetylacetone (*Ann. Chim. Phys.*, 1887, [vi], **12**, 215). In the present instance, however, only 1⅛ molecules of hydroxylamine were employed; 45 grams of hydroxylamine sulphate and 37·9 grams of potassium carbonate were added successively to 50 grams of acetylacetone dissolved in 800 c.c. of water, the mixture being heated under reflux for about two and a half hours. The progress of the condensation was indicated by a gradual fading of the ferric chloride coloration. The supernatant oil was removed, the aqueous layer extracted with ether, the extract concentrated, and the oily residue distilled, the distillate collected from 138—148° being rectified until a fraction was obtained boiling at 140—142°. The yield of *iso*oxazole was 84 per cent. of the calculated amount. This condensation was also effected by heating together acetylacetone (8 grams) and hydroxylamine sulphate (8·5 grams) in 20 c.c. of glacial acetic acid for four hours. The acid liquid, diluted with water, was neutralised with potassium hydroxide, and the *iso*oxazole was extracted and isolated as in the preceding preparation; the yield by this method was, however, only 60 per cent.

4-*Nitro*-3 : 5-*dimethyl*iso*oxazole* (formula I).—Thirty-two c.c. of concentrated sulphuric acid (D 1·84) and 15 grams of 3 : 5-dimethyl*iso*oxazole were slowly mixed, the temperature being kept below 0°; 16 c.c. of nitric acid (D 1·42) were slowly added, when the brown solution assumed a pale yellowish-green colour, and a further 64 c.c. of concentrated sulphuric acid were added, all these mixings being carried out below 0°. The solution was then left at the ordinary temperature overnight and finally warmed on the water-bath for one and a half hours, when nitrous fumes were evolved, but only in small amount. The solution was again cooled and poured on to ice, when the nitro-compound, separating in colourless flakes, was washed with ice-cold water, in which it was slightly soluble (1 gram in 200 c.c.). This dissolved portion was recovered by extraction with ether, the total yield being 86 per cent. of the calculated quantity.

4-*Nitro*-3 : 5-*dimethyl*iso*oxazole* crystallised from hot water or alcohol in transparent, hexagonal plates melting at 63·5°; it was very soluble in ether, benzene, or the alcohols (Found : N = 19·88, 19·65. $C_5H_6O_3N_2$ requires N = 19·72 per cent.). This nitro-compound was volatile in steam and appreciably volatile at the ordinary temperature; 0·3 gram left in a sulphuric acid desiccator disappeared completely, probably dissolving in the acid. With

coholic potassium hydroxide solution a yellow to reddish-brown ›loration was developed; the coloured product dissolved in benzene, ıt was insoluble in ether.

4-*Amino*-3 : 5-*dimethyl*iso*oxazole* (formula II).—The reduction of ıe foregoing nitro-compound was effected by using amalgamated luminium and moist ether, a method hitherto employed chiefly ı reducing aldehydes, ketones, and ethylene linkings.

About 3 grams of aluminium foil, amalgamated by immersion in ·queous mercuric chloride solution, were washed with water, and ·dded quickly, while moist, to 7 grams of 4-nitro-3 : 5-dimethyl*iso*-›xazole dissolved in 100 c.c. of moist ether. A vigorous evolution of ;as occurred, accompanied by a considerable rise of temperature, so ·hat the reduction flask had to be attached to a reflux condenser ınd cooled to prevent the ether boiling away too rapidly. After ·orty-five minutes another 3 grams of amalgamated aluminium were added and further additions of the reducing agent were made until reduction was complete, this result being indicated when a test portion gave no yellow coloration with alcoholic potassium hydroxide solution. The large excess of aluminium was used in order to complete the reduction within four hours. If a longer time elapsed, the product became discoloured. Only a slight proportion of water was employed, otherwise a separation of the liquid into two layers occurred and this immiscibility also diminished the rate of reduction.

The aluminium hydroxide and excess of aluminium having been filtered off, the filtrate and washings were concentrated under slightly reduced pressure, coal gas being bubbled through the liquid to prevent oxidation. The amine left behind as a pale brown oil solidified on cooling (yield = 70 per cent.).

4-*Amino*-3 : 5-*dimethyl*iso*oxazole*, after repeated crystallisation from equal parts of dry benzene and light petroleum, separated in colourless prisms melting at 56—57°; it was very soluble in water, ether, benzene, chloroform, or the alcohols, but dissolved only sparingly in light petroleum. In contact with moist air, the base became brown, but was comparatively stable when dry; it was slightly volatile in steam (Found: C = 53·33; H = 7·72; N = 25·05. $C_5H_8ON_2$ requires C = 53·54; H = 7·20; N = 25·00 per cent.).

4-*Amino*-3 : 5-*dimethyl*iso*oxazole Hydrochloride*, $C_5H_6ON\cdot NH_2,HCl$. —This salt was made either by adding the calculated quantity of concentrated hydrochloric acid to the base and evaporating to dryness or by passing hydrogen chloride through a solution of the amine in dry ether. It was obtained in colourless, prismatic needles by dissolving in absolute alcohol and adding dry ether

(Found: Cl = 24·01. $C_5H_8ON_2,HCl$ requires Cl = 23·86 per cent.). The hydrochloride, which was very soluble in water, alcohol, or chloroform but insoluble in ether, benzene, or petroleum, became brown in contact with moist air or in aqueous solution; it blackened at 142° and decomposed at 212—214°.

4-*Acetylamino*-3 : 5-*dimethyl*iso*oxazole*, $C_5H_6ON{\cdot}NH{\cdot}CO{\cdot}CH_3$, was prepared by mixing equal parts of the base and acetic anhydride. After evaporation in a vacuum desiccator, the residue crystallised from a large volume of light petroleum in transparent, colourless, prismatic needles melting at 108—109° (Found: N = 17·87. $C_7H_{10}O_2N_2$ requires N = 18·18 per cent.). The acetyl derivative dissolved very readily in water, alcohol, ether, acetone, or benzene, but only sparingly in light petroleum.

4-*Benzoylamino*-3 : 5-*dimethyl*iso*oxazole*, $C_5H_6ON{\cdot}NH{\cdot}CO{\cdot}C_6H_5$, obtained by the Schotten-Baumann process, crystallised from alcohol in rosettes of colourless needles melting at 190—191°; it was insoluble in water (Found: N = 12·48. $C_{12}H_{12}O_2N_2$ requires N = 12·97 per cent.).

4-Amino-3 : 5-dimethyl*iso*oxazole was condensed with benzaldehyde and its nitro-derivatives to yield the corresponding azomethine or Schiff bases.

General Method.—To 1 gram of the base dissolved in 40 c.c. of water was added the calculated amount of the aldehyde, sufficient alcohol being added, if necessary, to dissolve this reagent. The mixture, after heating under reflux for two hours, was cooled to complete the precipitation of the condensation product.

4-*Benzylideneamino*-3 : 5-*dimethyl*iso*oxazole*, $C_6H_5{\cdot}CH{:}N{\cdot}C_5H_6ON$, separated from a mixture of equal parts of alcohol and water in yellowish-white needles melting at 52—53°; it was soluble in benzene or ether (Found: N = 14·19. $C_{12}H_{12}ON_2$ requires N = 14·00 per cent.).

4-o-*Nitrobenzylideneamino*-3 : 5-*dimethyl*iso*oxazole*,

$$NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_5H_6ON,$$

crystallised from alcohol in pale greenish-yellow, prismatic needles intermediate in depth of colour between the meta- and para-nitro-isomerides; it melted at 124—125°, and was very soluble in benzene or hot alcohol (Found: N = 17·06. $C_{12}H_{11}O_3N_3$ requires N = 17·14 per cent.). This Schiff base on exposure to air assumed superficially a reddish-brown tint.

4-m-*Nitrobenzylideneamino*-3 : 5-*dimethyl*iso*oxazole* separated from alcohol in pale brownish-yellow, prismatic needles melting at 156—156·5°. It dissolved very readily in benzene, less so in alcohol, and was insoluble in water (Found: N = 16·85. $C_{12}H_{11}O_3N_3$ requires 17·14 per cent.).

4-p-*Nitrobenzylideneamino*-3 : 5-*dimethyl*isoo*xazole* crystallised from alcohol containing a small proportion of benzene in golden-yellow, prismatic needles melting at 184—185°. This Schiff base, the most highly coloured of the foregoing series, was very soluble in benzene, less so in alcohol (Found: N = 17·22. $C_{12}H_{11}O_3N_3$ requires N = 17·14 per cent.).

*3 : 5-Dimethyl*isoo*xazole-4-diazonium Salts.*

4-Amino-3 : 5-dimethyl*iso*oxazole was found to be diazotisable in hydrochloric, nitric, or sulphuric acid, quite like an aromatic primary amine. The diazonium salts with the foregoing mineral acids were very soluble in water; they decomposed in solution at the ordinary temperature and more rapidly on warming, so that they were much less stable than the 3 : 5-dimethylpyrazole-4-diazonium salts. Unless twice the theoretical amount of mineral acid was employed in the diazotisation of 4-amino-3 : 5-dimethyl*iso*oxazole, a brown, pasty solid separated, which was possibly an unstable diazoamino-compound, for it coupled with β-naphthol in alkaline solution. On the addition of sodium azide to a solution of 3 : 5-dimethyl*iso*oxazole-4-diazonium hydrochloride, a vigorous evolution of gas occurred, indicating the presence of a diazonium complex. The resulting 4-triazo-3 : 5-dimethyl*iso*oxazole was a pale yellow oil, which solidified in a mixture of ice and salt.

3 : 5-*Dimethyl*isoo*xazole-4-diazonium aurichloride* (formula III).—Sodium nitrite (0·8 gram) was added to a well-cooled solution of 1 gram of the amino*iso*oxazole in 5 c.c. of concentrated hydrochloric acid. The diazo-solution was added to an aqueous solution of 5·6 grams of sodium aurichloride (≡ 2·8 grams $AuCl_3$). A yellow precipitate was produced, coagulating to a pasty mass, which subsequently solidified; this product, which melted at 107—108°, was slightly soluble in water, alcohol, or chloroform (Found: Au = 42·03; Cl = 30·48; N = 8·56. $C_5H_6ON_3AuCl_4$ requires Au = 42·58; Cl = 30·62; N = 9·07 per cent.). Like the foregoing 3 : 5-dimethyl*iso*oxazole-4-diazonium salts, this aurichloride coupled with an alcoholic solution of β-naphthol, yielding orange needles of the corresponding azo-β-naphthol; when kept dry it retained this property for an indefinite time. When warmed with water, evolution of nitrogen occurred and concentrated sulphuric acid caused a vigorous effervescence.

The 3 : 5-dimethyl*iso*oxazole-4-diazonium salts also coupled readily with resorcinol and the naphthylamines.

3 : 5-*Dimethyl*isoo*xazole-4-azo-β-naphthol* (formula IV).—One gram of the amino*iso*oxazole was dissolved in hydrochloric acid and

diazotised as in the preceding preparation, the diazo-solution being added to 1·20 grams of β-naphthol dissolved in *N*/2-sodium hydroxide. A yellow precipitate was deposited forthwith, and a further amount obtained by salting out. When recrystallised from alcohol or glacial acetic acid, this azo-β-naphthol separated in dark orange needles melting at 202—203° (yield 86 per cent.); it was very soluble in benzene or glacial acetic acid, less so in alcohol, dissolved sparingly in aqueous ammonia or sodium hydroxide solution, but was insoluble in water (Found: C = 66·90; H = 5·33; N = 15·89. $C_{15}H_{13}O_2N_3$ requires C = 67·38; H = 4·90; N = 15·73 per cent.).

3 : 5-*Dimethyl*iso*oxazole*-4-*azoresorcinol* (formula V).—The diazo-solution prepared as before was freed from nitrous acid by the addition of urea and then added to an aqueous solution of resorcinol (1 mol.). The bright yellow precipitate, when crystallised from alcohol, yielded yellow needles melting at 217°; it was very soluble in benzene but insoluble in water (Found: N = 18·18. $C_{11}H_{11}O_3N_3$ requires N = 18·02 per cent.). Sulphuric acid developed with the azo-β-naphthol a deep carmine coloration and with the azoresorcinol an intense yellow tint.

3 : 5-*Dimethyl*iso*oxazole*-4-*azo*-β-*naphthylamine* (formula VI).—The diazo-solution from 4-amino-3 : 5-dimethyl*iso*oxazole hydrochloride, freed from excess of nitrous acid by urea, was added to β-naphthylamine (1 mol.) dissolved in 6 parts of glacial acetic acid. A voluminous, bright yellow precipitate was formed immediately, which on repeated crystallisation from alcohol was obtained in the form of brownish-red needles melting at 179—180° (Found: N = 21·10. $C_{15}H_{14}ON_4$ requires N = 21·05 per cent.).

The diazo-solution, when added to α-naphthylamine dissolved in glacial acetic acid, gave a red precipitate melting at 159°. This product developed with concentrated sulphuric acid an intense scarlet coloration, whereas the foregoing azo-β-naphthylamine dissolved in the acid to an intense orange solution.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for grants which have partly defrayed the expenses of this investigation.

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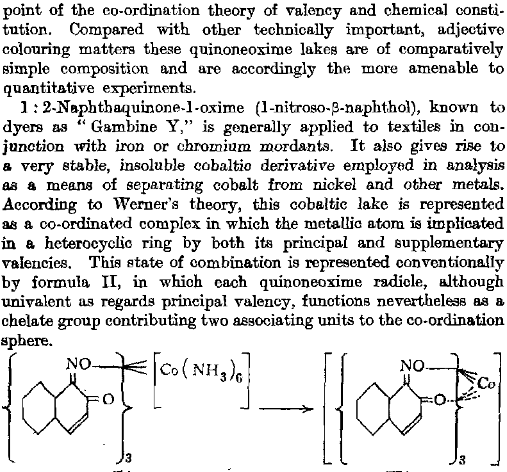
[*Received, March 24th*, 1921.]

LXXV.—*Researches on Co-ordination and Residual Affinity. Part IV. The Constitution of Simple and Complex Cobaltic Quinoneoxime Lakes.*

By Gilbert T. Morgan and J. D. Main Smith.

The metallic lakes of the orthoquinoneoximes form a group of mordant dyes which are of considerable interest from the view-point of the co-ordination theory of valency and chemical constitution. Compared with other technically important, adjective colouring matters these quinoneoxime lakes are of comparatively simple composition and are accordingly the more amenable to quantitative experiments.

1 : 2-Naphthaquinone-1-oxime (1-nitroso-β-naphthol), known to dyers as "Gambine Y," is generally applied to textiles in conjunction with iron or chromium mordants. It also gives rise to a very stable, insoluble cobaltic derivative employed in analysis as a means of separating cobalt from nickel and other metals. According to Werner's theory, this cobaltic lake is represented as a co-ordinated complex in which the metallic atom is implicated in a heterocyclic ring by both its principal and supplementary valencies. This state of combination is represented conventionally by formula II, in which each quinoneoxime radicle, although univalent as regards principal valency, functions nevertheless as a chelate group contributing two associating units to the co-ordination sphere.



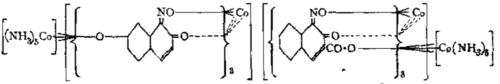
(I.) (II.)

By the experiments described below direct evidence has been obtained in support of the view that each chelate quinoneoxime radicle is the equivalent of two molecules of ammonia situated in the co-ordination complex of a cobaltammine such as $[Co,6NH_3]Cl_3$. When sodium 1 : 2-naphthaquinone-1-oximate and this hexamminocobaltic chloride interact at the ordinary temperature the sparingly soluble, dark green *hexamminocobaltic* 1 : 2-*naphthaquinone*-1-*oximate* (I) is precipitated. This substance, which is readily decomposed in the cold by aqueous alkalis regenerating

the alkali quinoneoximate, has the properties of an unstable cobaltic salt. When, however, this hexamminocobaltic derivative is gently warmed at 40°, *it loses completely all the ammonia of the co-ordination complex and passes quantitatively into the stable cobaltic lake* (II), from which the cobalt is no longer separable by such analytical reagents as the caustic or carbonated alkalis or ammonia. In this process three chelate groups have entered the co-ordination sphere in replacement of the six ammonia molecules. The resulting cobaltic lake no longer possesses any capacity for combining with ammonia, and hence it may be inferred that the ketonic limb of the chelate radicle, as well as the *iso*nitroso-group, is in direct association with the central cobalt atom.

A similar result is obtained by treating sodium 1 : 2-naphthaquinone-1-oximate with (purpureo-) pentamminocobaltic chloride, but with this difference, that the pentamminocobaltic salt of the quinoneoxime is unstable even at the ordinary temperature and evolves ammonia, passing forthwith completely into the cobaltic lake. These ammoniated cobaltic intermediate products are remarkably unlike hexa-amminocobaltic chloride, which begins to dissociate only at or above 173° (Clark, Quick, and Harkins, *J. Amer. Chem. Soc.*, 1920, **42**, 2483).

This complete saturation of the chemical affinity of the cobalt atom by three chelate quinoneoxime complexes is also demonstrated conclusively in the following direct manner, by selecting substituted quinoneoximes containing other salt-forming groups besides the quinoneoxime radicle. 7-Hydroxy-1 : 2-naphthaquinone-1-oxime, $HO{\cdot}C_{10}H_5O{:}NOH$, known also as 1-nitroso-2 : 7-dihydroxynaphthalene and "Gambine H," yields a simple cobaltic lake, $\left[\left\{HO{\cdot}C_{10}H_5{<}^{NO}_{O\cdots}\right\}_3Co\right]$, by reaction with a cobalt salt and air, but when it is subjected to the combined action of cobalt chloride, ammonia and hydrogen peroxide a greenish-black complex cobaltic lake (III) * is precipitated containing two cobalt atoms and five molecules of ammonia.



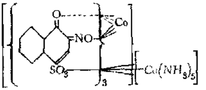
(III.) (IV.)

1 : 2-Naphthaquinone-1-oxime-3-carboxylic acid (1-nitroso-2-hydroxy-3-naphthoic acid), $CO_2H{\cdot}C_{10}H_5O{:}NOH$, furnishes a simple cobaltic lake, $\left[\left\{CO_2H{\cdot}C_{10}H_5{<}^{NO-}_{O\cdots}\right\}_3Co\right]$, when 2-hydroxy-3-

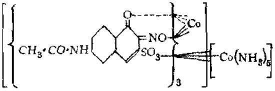
* See footnote following page.

naphthoic acid is acted on by nitrous acid in the presence of a cobalt salt, but when this lake is subjected to joint action of ammonia, hydrogen peroxide, and a cobalt salt a complex lake (IV) * is precipitated containing two cobalt atoms and five molecules of ammonia.

The nitroso-derivative of α-naphthol-4-sulphonic acid (1 : 2-naphthaquinone-2-oxime-4-sulphonic acid), $SO_3H\cdot C_{10}H_5O\colon NOH$, is used in conjunction with iron mordants as "Naphthol Green G" (B.D.C.). Its simple cobaltic lake, $\left[\left\{SO_3H\cdot C_{10}H_5{<}^{O\cdots}_{NO-}\right\}_3 Co\right]$, gives rise to a complex lake (V) * containing two cobalt atoms and five molecules of ammonia.



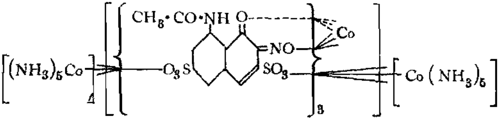
(V.)



(VI.)

6-Acetylamino-α-naphthol-3-sulphonic acid (acetyl J acid) gives rise to a nitroso(quinoneoxime) compound which furnishes either a simple or complex (VI) cobaltic lake. As in the preceding example, the complex lake contains two cobalt atoms and five molecular proportions of ammonia.

8-Acetylamino-α-naphthol-3 : 6-disulphonic acid (acetyl H acid) gives rise to a very soluble nitroso(quinoneoxime) derivative, which by the simultaneous action of cobaltous chloride, ammonia, and hydrogen peroxide furnishes a complex cobaltic lake (VII) containing three cobalt atoms and ten molecules of ammonia.

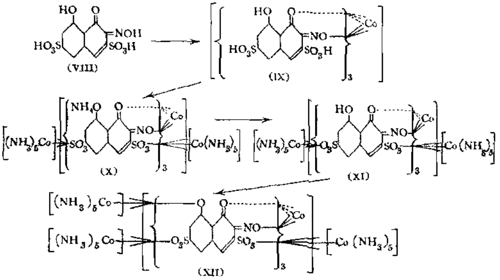


(VII.)

8-Hydroxy-1 : 2-naphthaquinone-2-oxime-3 : 6-disulphonic acid (VIII), from 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid

* In the graphic formulæ for the complex lakes (III, IV, V, VI, VII, X, XI, and XII) it should be understood that one acidic (oxy, CO_2, or SO_3) group out of three is implicated in the pentamminocobaltic co-ordination sphere, giving a co-ordination number of six. This relationship is represented conventionally by carrying one linking out of three into the co-ordination sphere.

(chromotrope acid), leads, according to the experimental conditions, to *one simple (IX) and one or other of three complex* lakes. The less complex lakes (X and XI) contain three cobalt atoms and ten ammonia molecules, whereas the other more complex lake (XII) contains four cobalt atoms and fifteen ammonia molecules.



In this increasingly complex series of cobaltic lakes it will be noticed that there is a constant ratio between the number n of cobalt atoms and the number m of ammonia molecules indicated by the equation, $m = 5(n - 1)$. This simple relationship demonstrates conclusively that in each of these complex lakes there is *one cobalt atom which is not capable of co-ordinating with ammonia.* Since the ratio of ammonia to the other cobalt atoms remains unchanged whether these cobaltic radicles replace the acidic hydrogen atoms of hydroxyl, carboxyl, or sulphonyl groups, it is evident that in these three states of combination the cobalt is still capable of co-ordinating with five molecules of ammonia. It may therefore be inferred that the cobalt atom in combination with the nitroso-group is the one which is completely saturated both as to principal valency and residual affinity (supplementary valency). In the compounds containing tervalent cobalt this condition is reached only when each cobalt atom is co-ordinated with six associated units, as in $[Co,6NH_3]Cl_3$, $K_3[Co(NO_2)_6]$, $K_3[Co(CN)_6]$ and many other substances of this series. Hence each quinoneoxime chelate group is the equivalent of two associating units and the cyclic constitution assigned to these lakes by Werner is thus confirmed by direct experiment.

EXPERIMENTAL.

Hexamminocobaltic 1 : 2-*Naphthaquinone*-1-*oximate* (*Hexamminocobaltic* 1-*Nitroso*-β-*naphthoxide*, Formula I).

Nitroso-β-naphthol (1·038 grams), dissolved in 6 c.c. of *N*-sodium hydroxide (3 mols.) and 10 c.c. of water, was treated in the cold with 0·535 gram of hexamminocobaltic chloride (luteocobaltic chloride), $[Co,6NH_3]Cl_3$, in 10 c.c. of water, when a dark sage-green, crystalline precipitate was obtained, leaving the solution almost colourless (Found: after drying in a vacuum desiccator, Co = 8·46; NH_3 = 14·56. $(C_{10}H_6O_2N)_3[Co,6NH_3]$ requires Co = 8·71; NH_3 = 15·07 per cent.). When warmed in water to about 40—50° this green ammoniocobaltic salt evolved 98·7 per cent. of the calculated amount of ammonia and turned quantitatively into red cobaltic 1 : 2-naphthaquinone-1-oximate. The bronzy green luteo-salt dissolved in aqueous solutions of ammonium and sodium hydroxides or the alkali carbonates to a greenish-yellow solution, from which, on boiling, cobaltic 1 : 2-naphthaquinone-1-oximate separated as a red precipitate.

When sodium nitroso-β-naphthoxide (1·28 grams) was treated with 0·50 gram of chloropentamminocobaltic dichloride (purpureocobaltic chloride), $[CoCl(5NH_3)]Cl_2$, in 70 c.c. of water, ammonia was evolved forthwith even in the cold and 99 per cent. of this gas was eliminated while the solution was being raised to the boiling point. The yield of cobaltic nitroso-β-naphthoxide was 99·5 pe cent. of the calculated amount.

1-*Cobaltic* 7-*hydroxy*-1 : 2-*naphthaquinone*-1-*oximate*.—2 : 7-Dihydroxynaphthalene (2·88 grams) was added to 0·35 gram o cobalt chloride and 1·66 grams of sodium nitrite in 18 c.c. of water the formation of a dark brown precipitate being accelerated b the addition of 6 c.c. of 2*N*-hydrochloric acid. The mixtur heated at 100° evolved nitric oxide; the precipitate (yield 88· per cent.), washed successively with water and ether, was drie over sulphuric acid (Found: Co = 8·55; N = 6·22; H_2O = 8·2 $Co(C_{10}H_6O_3N)_2,3H_2O$ requires Co = 8·71; N = 6·20; H_2O = 7·9 per cent.). The water is only eliminated at 150° in a vacuum.

The purple-brown lake with green reflex was sparingly solub in water, and readily so in aqueous alcohol or acetone to inten orange-red solutions; it dissolved in alkalis to an olive-blac solution, becoming reddish-orange on acidifying. Concentrate sulphuric acid developed an olive coloration, becoming red c dilution.

7-*Pentammino*-1 : 7-*dicobaltic* 7-*Oxy*-1 : 2-*naphthaquinone*-1-*oximate* (Formula III).

7-Hydroxy-1 : 2-naphthaquinone-1-oxime (3·10 grams) dissolved in excess of ammonia was treated with cobalt chloride (0·3 gram of Co) and 10 c.c. of 20 volume hydrogen peroxide. The liquid changed from purple to greenish-black and evolved oxygen; it was heated for fifteen minutes on the water-bath and cooled. The black precipitate was collected, washed with water and ether, and dried in a soda-lime desiccator (yield 74 per cent.) (Found: Co = 14·31; NH_3 = 10·40. $[Co(C_{10}H_5O_3N)_3][Co(NH_3)_5]3H_2O$ requires Co = 14·42; NH_3 = 10·39 per cent.).

The black dicobaltic lake dissolved in aqueous sodium hydroxide or concentrated sulphuric acid to an olive-green solution.

1-*Cobaltic* 1 : 2-*Naphthaquinone*-1-*oximate*-3-*carboxylic Acid*.—Sodium cobaltinitrite solution (380 c.c.) containing 0·74 gram of cobalt was added to β-naphthol-3-carboxylic acid (7·05 grams) dissolved in 200 c.c. of boiling absolute alcohol. After heating under reflux for six hours, 10 c.c. of concentrated hydrochloric acid were added and the dark purple precipitate was collected and dried at 100° (yield 75 per cent.) (Found: Co = 8·20; N = 6·04. $Co(C_{11}H_6O_4N)_3$ requires Co = 8·35; N = 5·94 per cent.).

The purplish-red lake was insoluble in water and sparingly soluble in acetone or alcohol to an orange solution; it readily dissolved in alkalis with intense reddish-yellow colour and was reprecipitated unchanged on acidifying. It dissolved in hot glacial acetic acid to a deep red solution and was deposited therefrom as a bright red powder on cooling. Concentrated sulphuric acid developed a reddish-brown colour, becoming yellow on dilution.

3-*Pentammino*-1 : 3-*dicobaltic* 1 : 2-*Naphthaquinone*-1-*oximate*-3-*carboxylate* (Formula IV).

1 : 2-Naphthaquinone-1-oxime-3-carboxylic acid (1·30 grams ≡ 3 mols.) was dissolved in 2 c.c. of 5*N*-ammonia (5 mols.) and 2 c.c. of aqueous cobalt chloride solution; the intensely red solution was warmed with hydrogen peroxide until oxygen was freely evolved. The addition of cobalt chloride, ammonia, and hydrogen peroxide was repeated and the mixture again warmed. The brown precipitate was collected after twelve hours, washed with ammonia and water, and dried in a soda-lime desiccator (yield 60 per cent.) (Found: Co = 13·67; NH_3 = 9·93; N* = 12·0. $[Co(C_{11}H_5O_4N)_3][Co(NH_3)_5]$ requires Co = 13·91; NH_3 = 10·02; N = 13·21 per cent.).

* The low nitrogen in this estimation was due undoubtedly to the fact that the compound evolved ammonia even in the cold.

The bright reddish-brown dicobaltic lake was slightly soluble in water to an orange solution, sparingly soluble in cold 5*N*-sodium hydroxide solution, but on heating it dissolved readily with evolution of ammonia to a greenish-yellow solution, becoming red on acidifying; it was soluble in aqueous alcohol, acetone, pyridine, concentrated sulphuric acid, or glacial acetic acid to intense red solutions, turning yellow with alkalis.

2-*Cobaltic* 1:2-*Naphthaquinone*-2-*oximate*-4-*sulphonic Acid*.—Owing to the extreme solubility of the cobaltic lake of 1:2-naphthaquinone-2-oxime-4-sulphonic acid, this compound was isolated in the form of its β-naphthylamine salt (compare Ambler, *J. Ind. Eng. Chem.*, 1920, **12**, 1081).

Sixty c.c. of 2*N*-sodium nitrite were added to a filtered solution of 25 grams of sodium α-naphthol-4-sulphonate (Nevile and Winther salt, 90 per cent.) in 200 c.c. of water; cobalt chloride (1·8 grams of Co) and 30 c.c. of 5*N*-hydrochloric acid were introduced successively, when the brown solution changed to blood red and evolved nitrous fumes. The solution, after being heated to boiling, was treated with β-naphthylamine, stirred vigorously for half an hour, cooled on ice, and the sparingly soluble precipitate dried in the air, extracted with ether, and dried again in an exhausted desiccator (yield 96 per cent.) (Found: Co = 4·91; N = 6·67; S = 7·31. $Co(C_{20}H_{15}O_5N_2S)_3$ requires Co = 4·74; N = 6·75; S = 7·72 per cent.).

The β-*naphthylamine* salt was a crystalline, bright red lake sparingly soluble in cold water or hydrochloric acid, dissolving readily in aqueous alkalis or concentrated sulphuric acid to deep red solutions.

4-*Pentammino*-2:4-*dicobaltic* 1:2-*Naphthaquinone*-2-*oximate*-4-*sulphonate* (Formula V).

The solution of the cobaltic compound of 1:2-naphthaquinone-2-oxime-4-sulphonic acid obtained as in the preceding preparation was neutralised with 18 c.c. of 5*N*-ammonia, and then treated with 30 c.c. of 2*N*-cobalt chloride, 24 c.c. of 5*N*-ammonia, and 20 c.c. of 20 volume hydrogen peroxide. The liquid, now containing purple precipitate, was warmed with a slight excess of ammonia then cooled to complete the deposition of the complex lake, which after washing and drying in a soda-lime desiccator had the appearance of a crystalline, reddish-purple powder (yield 84 per cent. (Found: Co = 12·40; NH_3 = 9·02; N = 11·64; S = 9·60.

$$[Co(C_{10}H_5O_5NS)_3][Co(NH_3)_5]$$

requires Co = 12·34; NH_3 = 8·89; N = 11·72; S = 10·04 per cent

The dicobaltic lake was soluble in water, aqueous alcohol,

acetone to red solutions; boiling with alkalis turned the liquid yellow with evolution of ammonia. Concentrated sulphuric acid developed a blood-red coloration unchanged on dilution.

2-Cobaltic 6-Acetylamino-1:2-naphthaquinone-2-oximate-3-sulphonic Acid, $\left[\left\{\begin{matrix}CH_3\cdot CO\cdot NH \\ SO_3H\end{matrix}\right\rangle C_{10}H_4 \left\langle\!\!\left\langle\begin{matrix}O \cdots \\ NO-\end{matrix}\right\}_3 Co\right.\right.\right]$.—This soluble cobaltic lake was also isolated as its sparingly soluble β-*naphthylamine* salt. Cobalt carbonate (2 grams) and 8·05 grams of sodium nitrite were dissolved in 60 c.c. of water and treated slowly with 4·0 grams of glacial acetic acid, the mixture being warmed at 40° until nitrous fumes were no longer evolved; 14·05 grams of 6-acetylamino-α-naphthol-3-sulphonic acid (acetyl J acid) were introduced and the mixture heated under reflux until the evolution of nitrous fumes again ceased. The intensely blood-red liquid, on cooling, set to a stiff paste, to which 12 c.c. of ice-cold 10*N*-hydrochloric acid were added. After twelve hours, the dark red paste was collected and dried on porous plate and afterwards at 100°. This cobaltic compound developed an intense orange-red coloration with concentrated sulphuric acid and a deep reddish-brown with alkalis; it was insoluble in organic solvents, but dissolved in wet acetone or in aqueous alcohol to a deep red solution.

Equal weights of β-naphthylamine (3 grams) and the cobaltic compound were mixed in 50 c.c. of boiling water, and the dark red precipitate, washed successively with water and ether, was obtained as a reddish-purple powder with bronzy reflex (Found: Co = 4·05; N = 9·06; S = 6·91. $Co(C_{22}H_{18}O_6N_3S)_3$ requires Co = 4·17; N = 8·90; S = 6·78 per cent.).

This β-naphthylamine salt was sparingly soluble in hot water and dissolved in cold aqueous sodium hydroxide to a deep red solution, which evolved ammonia on boiling and developed an intensely red coloration. The solution in concentrated sulphuric acid was olive-black, becoming successively purple and red on dilution.

The cobaltic nitrosoacetyl J acid, when refluxed for six hours with 2*N*-sodium hydroxide, became hydrolysed, losing its acetyl group. The product precipitated on addition of 10*N*-hydrochloric acid was a dark brownish-grey powder, soluble in water to a pink solution and in alkalis with a brown colour. It was insoluble in organic solvents. This cobaltic nitroso J acid,

$$Co\left[\begin{matrix}-NO \\ \cdots O\end{matrix}\!\!\gg C_{10}H_4(NH_2)\cdot SO_3H\right]_3,$$

was readily diazotised. The diazo-compound gave with β-naphthol an orange dye (on wool), with J acid a bluish-violet dye (on cotton), and with acetyl J acid a brick-red dye (on wool). The cobaltic

nitroso J acid yielded benzoyl and *p*-toluenesulphonyl derivatives on treatment with benzoyl chloride and sodium hydroxide or *p*-toluene-sulphonyl chloride and sodium acetate respectively.

The cobaltic lake of nitrosoacetyl J acid, when boiled with 5*N*-sodium hydroxide, lost the entire acetylamino-group (Found: $NH_3 = 3{\cdot}85$. $Co(C_{22}H_{18}O_6N_3S)_3$ requires $NH_3 = 3{\cdot}60$ per cent.).

3-*Pentammino*-2 : 3-*dicobaltic* 6-*Acetylamino*-1 : 2-*naphthaquinone*-2-*oximate*-3-*sulphonate* (Formula VI).

The solution of the simple cobaltic compound of 6-acetylamino-1 : 2-naphthaquinone-2-oxime-3-sulphonic acid (nitrosoacetyl J acid), prepared as in the preceding experiment, was neutralised with 16·7 c.c. of 5*N*-ammonia, treated with 10 c.c. of 2*N*-cobalt chloride, 13·3 c.c. of 5*N*-ammonia, and 17 c.c. of 20 volume hydrogen peroxide, and warmed at 50°, when the colour deepened considerably and a reddish-purple precipitate separated. This product was treated as in the case of the complex lake from Nevile and Winther acid (yield 64 per cent.) (Found: Co = 9·80; $NH_3 = 11{\cdot}27$; N = 13·20; S = 7·97; $H_2O = 5{\cdot}92$.

$$[Co(C_{12}H_8O_6N_2S)_3][Co(NH_3)_5]4H_2O$$

requires Co = 9·84; $NH_3 = 11{\cdot}35$; N = 12·85; S = 8·01; $H_2O = 6{\cdot}01$ per cent.).

This complex dicobaltic lake was only slightly soluble in water; it dissolved in cold caustic alkali to a deep red solution, becoming blood red and evolving ammonia on boiling. Concentrated sulphuric acid developed an intense brown coloration, becoming orange on dilution.

3 : 6-*Dipentammino*-2 : 3 : 6-*tricobaltic* 8-*Acetylamino*-1 : 2-*naphthaquinone*-2-*oximate*-3 : 6-*disulphonate* (Formula VII).

A few c.c. of 20 volume hydrogen peroxide were added to an aqueous solution (50 c.c.) of 12·2 grams of sodium 8-acetylamino-α-naphthol-3 : 6-disulphonate (acetyl H salt), 10 c.c. of 2N-cobalt chloride, 15 c.c. of 2N-sodium nitrite, and 35 c.c. of 2N-hydrochloric acid. The dark red solution was heated for fifteen minutes on the water-bath to complete the formation of the simple cobaltic compound. After cooling, 20 c.c. of 2N-cobalt chloride solution and a few c.c. of 20 volume hydrogen peroxide were added and the liquid rendered strongly alkaline with 18N-ammonia. After twelve hours in the ice-chest a brown precipitate was collected and treated as in the foregoing cases of complex cobaltic lake (yield 60 per cent.) (Found: Co = 11·27; NH_3 (pentammine) = 11·80; NH_3 (total) = 13·53; N = 14·74; S = 11·50; $H_2O = 2{\cdot}48$. $[Co(C_{12}H_7O_9N_2S_2)_3][Co(NH_3)_5]_2,2H_2O$ requires Co = 11·46; NH_3

(pentammine) 11·01; NH_3 (total) = 14·31; N = 14·51; S = 12·43; H_2O = 2·33 per cent.).

The total ammonia includes in addition to pentammine ammonia that derived from the nitrogen of the acetylamino-group.

The reddish-brown alkaline solution of the tricobaltic lake after hydrolysis became intensely bluish-purple and probably contained sodium 2-cobaltic 8-hydroxy-1 : 2-naphthaquinone-2-oximate-3 : 6-disulphonate (Formula IX). The solutions of the tricobaltic lake in aqueous mineral acids were reddish-violet, whereas concentrated sulphuric acid gave a blood-red coloration, becoming crimson on dilution.

8-Hydroxy-1 : 2-naphthaquinone-2-oxime-3 : 6-disulphonic Acid (Formula VIII).

β-Naphthylamine Salt.—The calculated amount of β-naphthylamine was added to an acid solution of this soluble quinoneoxime (nitroso) derivative of 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid (chromotrope acid), when the sparingly soluble salt was obtained as a reddish-purple precipitate (Found: N = 6·56; S = 7·76; H_2O = 2·45. $C_{40}H_{34}O_9N_4S_2,H_2O$ requires N = 7·04; S = 8·04; H_2O = 2·26 per cent.).

2-Cobaltic 8-Hydroxy-1 : 2-naphthaquinone-2-oximate-3 : 6-disulphonic Acid (Formula IX).

β-Naphthylamine Salt.—Sodium 1 : 8-dihydroxynaphthalene-3 : 6-disulphonate (5·9 grams of 80 per cent. acid salt), dissolved in 25 c.c. of water, was added to a solution of 4 c.c. of 2*N*-cobalt chloride and 8 c.c. of 2*N*-sodium nitrite; the brown mixture, after being acidified with 10 c.c. of 2*N*-hydrochloric acid, became red and evolved nitrous fumes. After the mixture had been stirred for thirty minutes and then warmed to 60°, the excess of nitrous acid was decomposed by the addition of 2 grams of urea and 3·4 grams of β-naphthylamine were introduced to the boiling solution. The *salt* (molecular weight 2015), which separated on cooling, was purified by washing successively with water and ether as in a former example (page 711) (Yield 58 per cent.) (Found: Co = 3·50; N = 6·26; S = 9·14; H_2O = 2·94. $[Co(C_{30}H_{24}O_9N_3S_2)_3]3H_2O$ requires Co = 2·93; N = 6·25; S = 9·53; H_2O = 2·68 per cent.).

8-Ammonium 3 : 6-Dipentammino-2 : 3 : 6-tricobaltic 8-Oxy-1 : 2-naphthaquinone-2-oximate-3 : 6-disulphonate (Formula X).

With the quantities indicated in the preceding experiment the blood-red, acid solution of 8-hydroxy-1 : 2-naphthaquinone-2-oxime-3 : 6-disulphonic acid, when rendered ammoniacal with

7·5 c.c. of 5*N*-ammonia, underwent a striking colour change to bluish-violet.

A solution consisting of 8 c.c. of 2*N*-cobalt chloride, 6·6 c.c. of 5*N*-ammonia, and 5 c.c. of 20 volume hydrogen peroxide was added to the foregoing solution, when a gelatinous indigo-blue precipitate was produced forthwith. The mixture was warmed with a slight excess of ammonia and then cooled to 0° and the dark blue precipitate was collected and treated as in former cases of complex lakes (yield 48 per cent.) (Found: Co = 11·92; NH_3 = 14·76; N = 14·82; S = 13·00; H_2O = 5·49.

$$[NH_4]_3[Co(C_{10}H_4O_9NS_2)_3][Co(NH_3)_5]_2,5H_2O$$

requires Co = 11·60; NH_3 = 14·48; N = 14·68; S = 12·58; H_2O = 5·90 per cent.).

This tricobaltic lake, a dark blue powder, was slightly soluble in boiling water to a pure blue solution, becoming red with acids; it dissolved in aqueous caustic alkalis to a deep blue solution, evolving ammonia in the cold. On warming, more ammonia was evolved and the liquid became a darker blue. Similar colour changes have been noted with acid and alkaline solutions of cobalt salts and nitrosochromotrope acid (Brenner, *Helv. Chim. Acta*, 1920, **3**, 90).

3 : 6-*Dipentammino*-2 : 3 : 6-*tricobaltic* 8-*Hydroxy*-1 : 2-*naphthaquinone*-2-*oximate*-3 : 6-*disulphonate* (Formula XI).

The foregoing ammonium compound was triturated with *N*/10-hydrochloric acid in excess; the deep blue colour changed to dark red, the sparingly soluble 8-hydroxy-derivative was collected, washed, and dried over sulphuric acid (Found: Co = 12·37; NH_3 = 11·89. $[Co(C_{10}H_4O_9NS_2)_3][Co(NH_3)_5]_3,5H_2O$ requires Co = 12·00; NH_3 = 11·53 per cent.).

This purplish-red lake was extremely sensitive to ammonia, which changed the colour to blue by producing the foregoing ammonium salt.

3 : 6 : 8-*Tripentammino*-2 : 3 : 6 : 8-*tetracobaltic* 8-*Oxy*-1 : 2-*naphthaquinone*-2-*oximate*-3 : 6-*disulphonate* (Formula XII).

Sodium 1 : 8-dihydroxynaphthalene-3 : 6-disulphonate (7·3 grams of acid sodium salt, 80 per cent.) was added to a solution consisting of 20 c.c. of 2*N*-cobalt chloride and 15 c.c. of 5*N*-ammonia, when an intensely purple liquid was obtained, which changed rapidly to intensely reddish-brown by aerial oxidation. Fifteen c.c. of 2*N*-sodium nitrite and 10 c.c. of 2*N*-cobalt chloride were added and the mixture cooled and acidified with glacial acetic acid, when the liquid assumed a deep reddish-purple colour and set slowly

to a stiff purplish-black paste. A large excess of ammonia was added, the mixture stirred for thirty minutes, and the precipitate collected and dried as in foregoing cases (yield 90 per cent.) (Found : Co = 14·90; NH_3 = 16·12; N = 15·47; S = 10·82; H_2O = 5·78. $[Co(C_{10}H_3O_9NS_2)_3][Co(NH_3)_5]_3,5H_2O$ requires Co = 14·60; NH_3 = 15·78; N = 15·59; S = 11·88; H_2O = 5·57 per cent.).

This complex tetracobaltic lake, a bluish-black, crystalline powder, was almost insoluble in water or organic solvents, and was insoluble in cold aqueous caustic alkalis, but on warming it dissolved to a dark purple solution, evolving ammonia.

Concentrated sulphuric acid with the two preceding lakes developed a violet coloration, becoming red on dilution, but with the tetracobaltic lake the colour was dark reddish-brown, becoming purplish-brown on dilution.

Appendix.

1. The dyeings produced with simple and complex metallic lakes of three of the naphthaquinoneoximes are tabulated in the first of the following tables.

2. The second table contains a list of colour reactions developed by means of sodium cobaltinitrite and the naphthols and the ten dihydroxynaphthalenes. These colorations, which are due to the formation of cobaltic naphthaquinoneoximates, are more distinctive than those produced with ferric chloride.

Adjective Dyeings with Quinoneoxime (Nitrosonaphthol) Dyes.

Name.	Metallic components of lakes.	Colour of lakes on wool.	Fastness to Light (L) and Scouring (S).
1 : 2-Naphthaquinone-1-oxime-3-carboxylic acid.	Cobalt and Aluminium	Dark salmon to red.	Fast to S, and fairly fast to L.
	Cobalt and Magnesium, Calcium, Barium	*Light* orange-fawn to brownish-orange.	Less fast to S.
,,	Iron and Aluminium	Dark sage to olive-green.	Fast to S and L.
	Iron and Calcium.	Yellow to dark green.	Less fast to S.
,,	Aluminium and Aluminium.	Light fawn to brown.	Fast to S, but not to L.
,,	Vanadic and ,,	Dark brown.	Fast to S.
,,	Vanadyl and ,,	Sage green.	Fast to S.
1 : 2-Naphthaquinone-2-oxime-4-sulphonic acid.	Cobalt.	Light plum red.	Not fast to S.
	,, and Aluminium.	Dark plum red.	Not fast to S, but fairly fast to L.
7-Hydroxy-1 : 2-naphthaquinone-1-oxime.	Cobalt.	Light to dark brown.	Not fast to S, but fairly fast to L.

Colour Reactions of the NAPHTHOLS *and* DIHYDROXYNAPHTHALENES *with Sodium Cobaltinitrite.*

	0·05 gram of compound, 1 c.c. *Mol*/15 *solution of* $Na_3Co(NO_2)_6$, 1 c.c. of 2*N*-acetic acid, 2 c.c. of water. Reaction on boiling.	Reaction after making alkaline with 2 c.c. of 2*N*-NaOH.	Reaction after acidifying with 3 c.c. of 2*N*-acetic acid.
Naphthol			
α-	Dark purple ppt.	Dark *purple* ppt. in *green* liquid, becoming deep *yellow* on boiling.	Ppt. unchanged, liquid becoming *yellow*.
β-	Dark purple ppt.	Dark *purple* ppt. in faintly *yellow* liquid, becoming *green* on boiling.	Ppt. unchanged, liquid becoming *olive-green*.
Dihydroxy-naphthalene			
1 : 2	Orange coloration and slight brown ppt.	Transient *purple* changing to *intense green* coloration.	Gelatinous *purplish-brown* ppt.
1 : 3	Reddish-purple ppt.	*Intense anatto yellow* coloration.	Gelatinous *yellowish-brown* ppt.
1 : 4	Very slight light brown ppt. in yellow liquid.	Dark *purplish-brown* coloration.	Gelatinous bright *reddish-violet* ppt. on standing.
2 : 3	Dark purple ppt.	*Intense* dark *brownish-yellow* coloration.	Gelatinous *purplish-brown* ppt.
1 : 5	Purplish-brown ppt.	*Intense* dark *reddish-purple* coloration.	Gelatinous *brownish-purple* ppt
1 : 6	Purplish-brown ppt.	*Intense blood-red* coloration.	Gelatinous bright *red* ppt.
1 : 7	Greenish-black ppt.	*Intense* dark *brown* coloration.	Gelatinous *olive black* ppt.
1 : 8	Purplish-black ppt.	*Intense* dark *violet* coloration.	Gelatinous *purpl* ppt.
2 : 6	Dark purplish-brown ppt.	*Intense purplish-black* coloration, becoming dark *purple* on dilution.	Gelatinous *purplish-red* ppt.
2 : 7	Dark purplish-brown ppt.	*Intense purplish-green-black* coloration, becoming dark *green* on dilution.	Gelatinous brigh *red* ppt.

The authors desire to express their thanks to the Advisor Council for Scientific and Industrial Research fcr grants whic have partly defrayed the expenses of this investigation.

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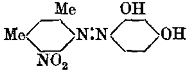
[*Received, March 24th,* 1921.]

LXXVI.—*Derivatives of m-Xylene.*

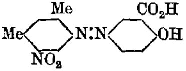
By Sydney Albert Pearman.

The experiments described below had for their object the study of *m*-xylene derivatives likely to be of use as colour-producing intermediates.

The starting-point was 6-nitro-*m*-4-xylidine, prepared by the nitration of *m*-4-xylidine by Noelting and Collin's method (*Ber.*, 1884, **17**, 265). The product, obtained in quantitative yield, was a mixture of the 2-nitro- and 6-nitro-derivatives of *m*-4-xylidine. Repeated extraction with boiling light petroleum (b. p. 40—60°) removed the greater part of the 2-nitro-compound, of which 32 grams were obtained from the product of nitration of 265 grams of *m*-4-xylidine. 6-Nitro-*m*-4-xylidine was purified by repeated crystallisation from alcohol; it then melted at 123° and was used in the following preparations:



(I.)



(II.)

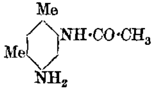
6-*Nitro*-m-*xylene*-4-*azoresorcinol* (I).—The ice-cold diazo-solution prepared from 3·3 grams of 6-nitro-*m*-4-xylidine, 12 c.c. of concentrated hydrochloric acid, 150 c.c. of water, and 2 grams of sodium nitrite was added to 250 c.c. of water containing 2·2 grams of resorcinol and 16 grams of sodium hydroxide. The sodium salt of the azo-dye was salted out after twelve hours; the azo-resorcinol set free with dilute sulphuric acid was crystallised from glacial acetic acid, when it separated in small, light red, iridescent, tabular crystals charring at 230° and intumescing at 248° (Found: N = 14·47. $C_{14}H_{13}O_4N_3$ requires N = 14·63 per cent.). This azo-compound dyes chromed wool in full orange shades.

The *diacetyl* derivative, produced by adding one drop of concentrated sulphuric acid to a solution of the azo-resorcinol in acetic anhydride, crystallised from alcohol in lustrous, orange-red flakes melting at 145—147° (Found: N = 11·63. $C_{18}H_{17}O_6N_3$ requires N = 11·32 per cent.).

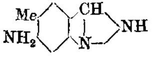
A lower homologue of the foregoing azo-resorcinol has recently been described by Leonard and Browne as a yellow, amorphous powder melting at 234° (*Sci. Proc. Roy. Dubl. Soc.*, 1920, **16**, 108); it has now been obtained in crystalline form.

*6-Nitro-*m*-xylene-4-azosalicylic Acid* (II).—The diazo-solution from 5 grams of 6-nitro-*m*-4-xylidine was added to a dilute sodium hydroxide solution of salicylic acid (4·6 grams); the deep red sodium salt of the dye was salted out. The dye, which is a homologue of Alizarin Yellow 2G, when set free by dilute sulphuric acid, was deposited as a brick-red, amorphous precipitate sintering at 210° and decomposing at 220—224° (Found: N = 12·72. $C_{15}H_{13}O_5N_3$ requires N = 13·33 per cent.). Concentrated sulphuric acid developed an orange-yellow coloration with the foregoing azo-resorcinol and a deep orange shade with the azo-salicylic acid. The latter also dyed chromed wool in deep yellow shades.

*Acetyl-4 : 6-diamino-*m*-xylene* (III).



(III.)



(IV.)

—Twenty-five grams of *acetyl-6-nitro-*m*-4-xylidine* (m. p. 159—160°) were reduced with 50 grams of zinc dust in 350 c.c. of 50 per cent. alcohol containing 5 grams of ammonium chloride. The reducing agent was added in three portions; the liquid was heated under reflux for two hours and filtered hot. On cooling, 20 grams of crude reduction product separated and were crystallised repeatedly from hot water. *Acetyl-4 : 6-diamino-*m*-xylene* then separated in stout needles having a bronzy reflex when moist and becoming opaque and white when dry; from benzene, it crystallised in colourless, matted needles melting at 164—166° (Found: C = 67·48; H = 7·61; N = 16·10. $C_{10}H_{14}ON_2$ requires C = 67·42; H = 7·87; N = 15·73 per cent.).

*6-Acetylamino-*m*-xylene-4-azo-β-naphthol,*

$$CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_2Me_2{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH,$$

crystallised from glacial acetic acid in matted, scarlet needles not melting below 300° (Found: N = 12·49. $C_{20}H_{19}O_2N_3$ requires N = 12·61 per cent.). This azo-derivative developed a magenta coloration with concentrated sulphuric acid, whereas the corresponding azo-phenol gave a deep orange-red shade.

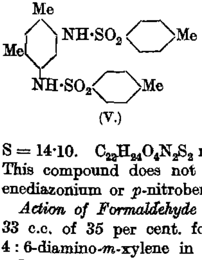
6-Amino-5-methylindazole (IV).—6-Nitro-5-methylindazole (2 grams) prepared according to Noelting's method (*Ber.*, 1904, **37**, 2588) and crystallised from hot water, was dissolved in 150 c.c. of 50 per cent. alcohol and treated successively with a solution of 20 grams of ferrous sulphate in 100 c.c. of water and excess of

aqueous ammonia. The mixture was heated under reflux for three hours, filtered hot, and concentrated, when 1·2 grams of 6-*amino*-5-*methylindazole* separated (yield 71 per cent.). This product crystallised from alcohol in hexagonal plates, from benzene in lustrous, colourless needles, both forms melting at 241—242° (Found: C = 65·85, 65·94; H = 6·18, 6·17; N = 28·98. $C_8H_9N_3$ requires C = 65·31; H = 6·12; N = 28·57 per cent.).

6-Amino-5-methylindazole dissolved readily in dilute mineral acids or alcohol; it was moderately soluble in hot water, but only sparingly soluble in boiling benzene. When moistened with alcohol, its odour resembled that of tobacco. The diazonium chloride from this aminoindazole gave a dark red, insoluble azo-β-naphthol and a violet azo-dye with J-acid.

6-Amino-5-methylindazole dissolved in dilute hydrochloric acid coupled with *p*-nitrobenzenediazonium chloride to form an insoluble scarlet azo-compound, the diazo-group probably becoming attached at position 3 in the indazole ring.

Di-p-*toluenesulphonyl*-4 : 6-*diamino*-m-*xylene* (V) was obtained by grinding together in a warm mortar 4 : 6-diamino-*m*-xylene (4·75 grams), *p*-toluenesulphonyl chloride (2·2 mols.), and fused sodium acetate (4 mols.) and decomposing the excess of the sulphonyl chloride by warming with sodium carbonate solution. The crude product (13·2 grams) was purified by dissolution in sodium hydroxide solution and precipitation with acetic acid. On crystallisation from alcohol, the sulphonamide was obtained in small, white needles melting at 221—222° (Found: N = 6·45; S = 14·10. $C_{22}H_{24}O_4N_2S_2$ requires N = 6·31; S = 14·41 per cent.). This compound does not couple in alkaline solution with benzenediazonium or *p*-nitrobenzenediazonium chloride.



(V.)

Action of Formaldehyde on 4 : 6-*Diamino*-m-*xylene*.—On adding 33 c.c. of 35 per cent. formaldehyde solution to 12·2 grams of 4 : 6-diamino-*m*-xylene in 180 c.c. of cold water, a voluminous, pale yellow precipitate separated suddenly. Concentrated sulphuric acid (6 c.c.) was added to dissolve the precipitate completely and subsequently the pale red solution began slowly to deposit pale pink, heavy, cubical crystals. After seven days this product (*A*), a sulphate, weighed 13·8 grams. The mother liquor from the sulphate precipitation was rendered ammoniacal, when a slimy pink precipitate (*B*), weighing 2·5 grams, was obtained, which, when boiled with hydrochloric acid and phloroglucinol, gave the brick-red insoluble phloroglucide (Clowes and Tollens, *Ber.*, 1899, **32**, 2841),

thus showing the characteristic behaviour of a Schiff base. The *sulphate A*, crystallised from alcohol, was sparingly soluble in the boiling solvent and separated therefrom in clusters of minute, white, hairy needles reddening at 200° and decomposing at 248° (Found: N = 13·72, 13·51; S = 7·81, 7·45. $[C_{10}H_{12}N_2]_2,H_2SO_4$ requires N = 13·40; S = 7·66 per cent.). The base liberated from the sulphate by ammonia was crystallised successively from alcohol, benzene, and petroleum (b. p. 65—75°), when it was obtained in snow-white needles resembling asbestos fibres and melting at 223·5—226° (Found: C = 74·39, 74·50; H = 7·16, 7·25; N = 17·14, 17·20. $C_{10}H_{12}N_2$ requires C = 75·00; H = 7·50; N = 17·50 per cent. Molecular weight determinations by the ebullioscopic method in benzene (0·981 and 2·003 grams per 100 c.c. respectively) gave M = 362, 336. $[C_{10}H_{12}N_2]_2$ requires M = 320).

On warming the amine with acetic anhydride, a *monoacetyl* derivative was produced, crystallising from glacial acetic acid in clusters of colourless prisms (Found: N = 14·42, 14·72. $C_{12}H_{14}ON_2$ requires N = 13·86 per cent.). These results, although not very close, corroborate the preceding data.

The base on treatment with nitrous acid gave a flocculent, yellow, unstable nitrosoamine, which decomposed at about 40° and could not be crystallised. It was not found possible to regenerate formaldehyde from the base, which remained unchanged on boiling with hydrochloric acid and phloroglucinol, giving no red phloroglucide. When mixed with 30 per cent. sulphuric acid and distilled in steam, the base was unaltered and formaldehyde could not be detected in the distillate.

This base (from product *A*) gave a red precipitate of selenium on treatment with selenium acetylacetone, whereas the Schiff base did not interact with this reagent for primary and secondary bases (compare Morgan and Drew, this vol., p. 610).

When the base, $C_{20}H_{24}N_4$, was treated at 150—160° with hydrochloric acid in a sealed tube and the product oxidised with ferric chloride and precipitated as a double salt with zinc chloride, a resinous product was obtained, which dyed wool in full orange shades. This condensation product was evidently a colouring matter of the acridine series.

The foregoing reactions show that the condensation product of 4 : 6-diamino-*m*-xylene and formaldehyde is a complex substance differing considerably in properties from the methylene compounds obtained from tolylene-2 : 4-diamine and *m*-phenylenediamine.

The author's thanks are due to the Research Grant Committee of the Chemical Society for a grant which has defrayed the expense

of this investigation, to the British Dyestuffs Corporation, Ltd. (Manchester), for the opportunity of carrying out the research, and to Professor G. T. Morgan for his interest in the work.

THE CHEMICAL DEPARTMENT,
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EDGBASTON. [*Received, March 24th*, 1921.]

LXXVII.—*Some Physico-chemical Problems connected with the Stability of Explosives.*

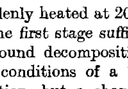
By CYRIL NORMAN HINSHELWOOD.

THE object of this paper is to deal with the thermal decomposition of high explosives from the point of view of chemical dynamics. In a recent paper (T., 1920, **117**, 1432) Farmer has described an experimental method for the measurement of the velocity of decomposition of high explosives. In a second paper (T., 1920, **117**, 1603) he describes its application as a stability test to control the manufacture of Service explosives, and deals in detail with the case of trinitrophenylmethylnitroamine (tetryl). At the time when the investigation described in the present paper was commenced, the author was unacquainted with Farmer's work (except as regards the apparatus of the Service test which was used in most of the measurements) and also worked on the nature of the decomposition of tetryl. In some respects, which will be briefly indicated in due place, this work simply confirmed that of Farmer, but in others the method of attack was different, so that it seems desirable to publish the results.

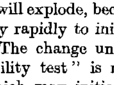
As stated by Farmer (*loc. cit.*), explosives undergo a slow decomposition at a temperature far below that at which they fire or detonate. For the practical estimation of stability the initial stages of decomposition are of most interest, but clearer light is thrown on the nature of the change by following it over its whole course. Fig. 1 shows the decomposition of molten tetryl at 140° and 150°. The evolution of gas ceases at approximately two gram-molecules per gram-molecule of tetryl and the non-gaseous residue amounts to 73 per cent. When an explosive detonates, it is resolved almost entirely into gaseous products and amorphous carbon, so that evidently the gradual decomposition is a much less profound change and does not consist in a complete disintegration of the molecule into products resembling the products of detonation.

In the case of tetryl, a large proportion of picric acid was extracted from the syrupy product, so that the benzene nucleus remained to a considerable extent intact. These facts throw some light on the mechanism of the explosion of tetryl. This is evidently to be regarded as a process taking place in steps rather than as the shattering of the molecule in a single process. The product of the completed slow decomposition at, say, 150° may be heated at well above 200° without decomposing further, yet if tetryl itself is suddenly heated at 200° it will explode, because heat will be evolved in the first stage sufficiently rapidly to initiate a further and more profound decomposition. The change undergone by tetryl under the conditions of a "stability test" is not the actual explosive reaction, but a change which may initiate this if it takes place sufficiently rapidly. Although complicated from the point of view of organic chemistry, the reaction is simple dynamically. It is unimolecular and autocatalytic, and is readily expressed by dynamical equations. Farmer suggests that the picric acid is partly responsible for the autocatalysis in the initial stages of the decomposition of molten tetryl. Experiments over the complete range of the decomposition with and without the addition of picric acid show that the autocatalysis is quantitatively accounted for by the production of this compound in the reaction.

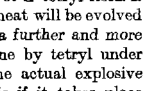
2 : 4 : 6-Trinitro-3-hydroxyphenylmethylnitroamine was also investigated. This compound is interesting because it embodies in one molecule the characteristic gronps both of tetryl and of picric acid.



Tetryl.



Picric acid.



Trinitrohydroxyphenylmethylnitroamine.

In virtue of its hydroxyl group it exerts an action similar to the catalytic action of picric acid on tetryl, whilst in virtue of the nitroamino-group it is unstable itself, and its instability is enhanced by the influence of its own hydroxyl group to about the same extent as the instability of tetryl is increased by picric acid. The additive relation found in the decomposition velocities of these compounds suggests that we may here be dealing with an instance of hydrion catalysis in a substance in the fused state.

On account of its practical significance the decomposition of solid tetryl was studied and special attention directed to an analysis of the form of the initial accelerated parts of the curves shown in Fig. 4. Extrapolation of the values found for molten tetryl to

lower temperatures had revealed a large difference between the velocity of decomposition in the liquid and in the solid states. As, however, a detailed account of work on similar lines has been recorded by Farmer, the results are not given in this paper. It is shown, however, that from the curve giving the depression of the melting point of tetryl by its decomposition products the acceleration in the rate of decomposition of the solid due to progressive melting may be quantitatively accounted for.

The hydroxy-analogue of tetryl shows a similar behaviour, its rate of decomposition increasing enormously when it becomes liquid.

Prof. Lewis suggested to the author that this difference in reactivity of the substance in the solid and in the liquid states should be expected, since there is a difference in internal energy between the two states equal to the latent heat of fusion. Quantitative investigation on the basis of this idea leads to an important result, namely, tetryl even after the most careful purification probably still contains small amounts of impurity which largely determine its rate of decomposition (as a solid) by giving rise to traces of liquid phase. The reaction in the case of molten tetryl is unimolecular, and assuming that a molecule decomposes when it possesses a "critical increment" of energy E_l we have from the Marcellin-Rice equation

$$\frac{d \log k_l}{d\theta} = \frac{E_l}{R\theta^2} \, .$$

If we now *assume* the reaction in the solid state to be homogeneous and unimolecular, we have

$$\frac{d \log k_s}{d\theta} = \frac{E_s}{R\theta^2} \, ,$$

where E_s is the critical increment for the reaction in the solid state. Then for the ratio of k_l to k_s at a given temperature we have

$$\log \frac{k_l}{k_s} = \frac{E_s - E_l}{R\theta} \, .$$

Now $E_s - E_l$ should equal λ, the latent heat of fusion per gram-molecule.

The latent heat of fusion was measured in the case of tetryl and found to be approximately 5,600 cals. This gives for k_l/k_s at 120° the value 1,300 approximately. In order to eliminate the effect of autocatalysis in the liquid state and of progressive melting in the solid we may take initial rates of decomposition as propor-

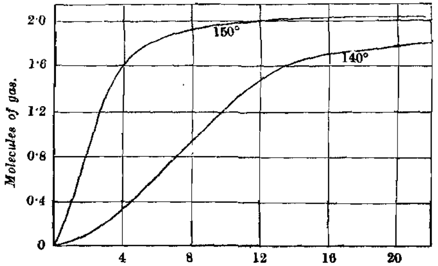
tional to velocity constants. Thus, assuming the reaction in the *solid state to be a homogeneous one, the solid should decompose* 1,300 times more slowly than the liquid at the same temperature. But the value 1,300 is a lower limit, since it has been shown by Hinshelwood and Bowen (*Phil. Mag.*, 1921, [vi], **40**, 569) that, in reactions where a gas is evolved from a solid, only those molecules in the neighbourhood of the surface of the solid decompose, and this would obviously make the relative rate of reaction in the solid state slower still. Now since the rate of reaction in the solid state is only about 50 to 100 times less than that in the liquid (in the case of tetryl at 120°), we must assume that even after the most careful purification the tetryl still contains traces of impurity which either give rise to liquid or exert some catalytic effect.

EXPERIMENTAL.

1. *Dynamics of the Complete Course of the Decomposition of Molten Tetryl.*

Measurements were made at 140° and 150°, quantities of about 0·1 gram of tetryl being used. *Fig. 1 shows the results obtained.*

FIG. 1.



Complete course of the decomposition of molten tetryl.

In order to express the change by an equation it was first necessary to determine the order of the reaction. The autocatalytic influence of the products makes it impossible to do this merely from the shape of the curve. It was found, however, that the rate at which tetryl decomposed when dissolved at different concentrations in pure

trinitrotoluene was the same as when it decomposed alone. Hence it may be taken that the reaction is unimolecular.

Time in hours.	*Molecules of gas from one molecule of tetryl.* Pure tetryl.	33% tetryl in molten trinitrotoluene.	16·6% tetryl in molten trinitrotoluene.
1	0·18	0·23	0·19
2	0·49	0·63	0·54
3	0·86	1·00	0·84
4	1·19	1·28	1·09
5	1·46	1·50	1·30
6	1·64	1·65	1·43

On the simplest assumption that the products of the reaction catalyse the reaction in direct proportion to their amount, the change will be represented by the equation

$$\frac{dx}{dt} = (k_1 + k_2x)(m - x)$$

where m = the total amount of gas evolved when the reaction has run its course, and x = the amount of gas evolved at time t. This gives on integration

$$\frac{1}{t} \log \frac{m}{m - x} + \frac{1}{t} \log (1 + Kx) = \text{constant},$$

where $k_2/k_1 = K$.

In an experiment with pure tetryl at 140° the total amount of gas was 1·95 mols., that is, $m = 1{\cdot}95$. When $t = 5$ (hours), $x = 0{\cdot}499$, and when $t = 10$, $x = 1{\cdot}31$. *Hence K is found to be* 5·34 and

$$\frac{1}{t} \log \frac{1{\cdot}95}{1{\cdot}95 - x} + \frac{1}{t} \log (1 + 5{\cdot}34x) = \text{constant} = S.$$

Substituting experimental values of t and x we find,

t.	x.	S (for decimal logs).
5·0, 10·0	0·499, 1·31	0·139
4·0	0·332	0·132
7·0	0·83	0·138
12·0	1·55	0·138
15·0	1·72	0·130

In a similar experiment at 150°, the following results were obtained:

$$m = 2{\cdot}01; \ K = 2{\cdot}78.$$

The values of S for different values of t and x were 0·374, 0·372, 0·371, 0·343, 0·336. Taking the constant as 0·37, we find

t.	x (calculated).	x (observed).
1·00	0·34	0·35
2·00	0·87	0·83
3·00	1·31	1·30
4·00	1·66	1·63
5·00	1·84	1·78
15·0	2·01	1·95
20·0	2·01	2·01

It is noteworthy that the decomposition of an explosive should follow so simple a law.

The isolation of picric acid from the products by extraction with water and repeated crystallisation has been mentioned. This affords another method of following the course of the reaction. A weighed amount of tetryl was allowed to decompose for a certain time and the acid formed was extracted and titrated. In an experiment at 140° the following results were obtained.

Hours of heating.	0·500 Gram taken in a number of tubes. C.c. of $N/20$-alkali required.
2·0	1·4
3·0	2·25
6·0	7·7
7·75	9·9
11·0	12·5
17·0	15·2

These values lie on a curve similar to that representing the gas evolution.

2. *Dynamics of the Decomposition of Molten Tetryl in Presence of Picric Acid.*

At 140°, the rate of decomposition of picric acid itself is very small compared with that of tetryl, and need not be taken into account. If the autocatalysis observed in the decomposition of tetryl is due to the picric acid formed, then the velocity in presence of a moderate quantity of added picric acid should be given by

$$\frac{dx}{dt} = k(a + x)(b - x)$$

where a = the amount of picric acid added and b = the amount of tetryl initially present.

For equimolecular proportions of tetryl and picric acid the integrated form of this becomes

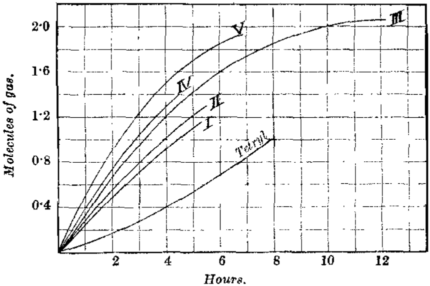
$$k = \frac{1}{2bt} \log \frac{b + x}{b - x}.$$

The following results illustrate this. They refer to an equimolecular mixture at 140°.

t (hours).	x (c.c.).	k.
0·50	0·66	0·071
1·00	1·39	0·0749
2·00	2·72	0·0751
3·00	3·98	0·0761
5·17	6·02	0·0752
6·00	6·59	0·0749
7·00	7·21	0·0757
8·50	7·83	0·0754
27·0	9·01	—

The influence of varying amounts of picric acid is shown in Fig. 2. In presence of excess of picric acid the autocatalytic influence of that produced in the reaction should be masked by that initially

FIG. 2.



Decomposition of tetryl in presence of varying amounts of picric acid.

I. 4 *mols. of tetryl,* 1 *mol. of picric acid.*
II. 2 ,, ,, 1 ,, ,,
III. 1 ,, ,, 1 ,, ,,
IV. 1 *mol. of tetryl,* 2·84 *mols. of picric acid.*
V. Excess of picric acid.

added and the reaction should obey the simple unimolecular law. This expectation is accurately fulfilled.

0·0802 Gram of tetryl in presence of 1·00 gram of picric acid.

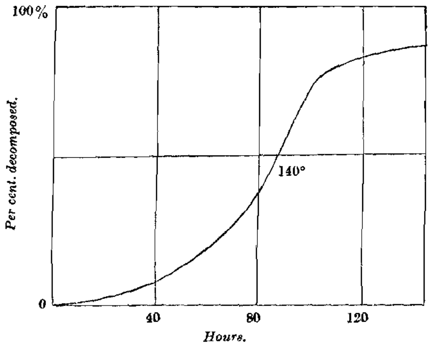
t (hours).	x (c.c.).	k (for simple unimolecular reaction).
0·50	1·07	—
2·00	5·43	0·0940
2·50	6·61	0·0972
3·05	7·78	0·1000
3·75	8·97	0·1009
4·00	9·32	0·1007
5·10	10·66	0·1001
6·00	11·65	0·1019
21·0	15·42	—

3. *Behaviour of the Hydroxy-analogue of Tetryl—2 : 4 : 6-Trinitro-3-hydroxyphenylmethylnitroamine.*

Fig. 3 shows the behaviour of this compound at 140°. It has a higher melting point (182°) than tetryl (129°) and is therefore solid at 140°, but it melts as decomposition proceeds. The fusion is accompanied by the usual increase in velocity of reaction. Like

that of tetryl, *its velocity of decomposition is accelerated* by picric acid. Since the velocity of decomposition of tetryl at 140° is not increased by admixture of trinitrotoluene, it is reasonable to suppose that that of the analogous hydroxy-compound will not be also.

FIG. 3.



Decomposition of trinitrohydroxyphenylmethylnitroamine.

The compound was therefore dissolved in several times its weight of fused trinitrotoluene and the gas evolution measured. Equimolecular mixtures of picric acid and the hydroxy-compound and of tetryl and the hydroxy-compound were also examined.

	Initial rate of decomposition in mols. per hour.
Hydroxy-compound (1 mol.) + tetryl (1 mol.)	0·70
Hydroxy-compound alone (molten in trinitrotoluene solution)	0·42
Difference, representing the rate of decomposition of tetryl catalysed by the hydroxy-compound	0·28
Compare tetryl + picric acid (1 mol.)	0·34
,, ,, + ,, ,, (½ mol.)	0·24

Thus the catalytic activity of the hydroxy-compound is approximately equal to that of picric acid.

The total gas evolved from the hydroxy-compound was 3·46 mols.; therefore,

$$\text{the initial rate} = \frac{0{\cdot}42 \times 100}{3{\cdot}46} = 12{\cdot}1 \text{ per cent. per hour.}$$

The total gas evolved from tetryl + 1 mol. of picric acid was 2·20 mols.; therefore,

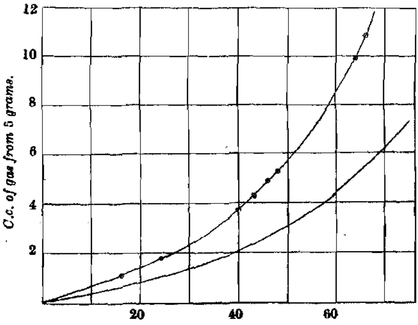
$$\text{the initial rate} = \frac{0{\cdot}34 \times 100}{2{\cdot}20} = 15{\cdot}4 \text{ per cent. per hour.}$$

Thus the rate of decomposition of the hydroxy-derivative approximates to that of tetryl in presence of 1 mol. of picric acid. In these results an additive relation is evident. The catalytic activity of both picric acid and the methylnitroaminopicric acid is clearly due to the hydroxyl group; both these compounds dissociate strongly in solution (the conductivity of the nitroamine is not recorded in the literature, but was found by the author to correspond witb a dissociation of about 98 per cent. at $N/200$ dilution) and since substances which ionise easily in solution usually ionise in the molten state, the additive relation found for the velocity of decomposition in the various cases suggests that we may be here dealing with a case of hydrogen-ion catalysis in substances in the fused state.

4. *The Initial Stages in the Decomposition of Solid Tetryl at* 120°.

In the initial stages, the decomposition of solid tetryl is strongly accelerated. A special study was made of the dynamics of this

FIG. 4.



Initial stages in the decomposition of solid tetryl.

part of the change. Farmer says (*loc. cit.*) that the acceleration is to a great extent due to progressive melting. The analysis now to be given of the curves (see Fig. 4) shows that the acceleration is

connected quantitatively with the production of the liquid phase due to the lowering of the melting point by the decomposition products.

Since the range of the decomposition to be studied is limited—involving only a few units per cent. of the tetryl present—we may neglect variations in the amount of undecomposed material.

Consider 1 gram of solid tetryl at 120°. The gas evolution depends on the following factors :

1. The initial rate of decomposition of the solid, denoted by v_1 (expressed in c.c. per gram per hour).

2. The amount of liquid phase introduced when an amount x of the tetryl has decomposed, denoted by $f(x)$. This will decompose at a rate v_2.

3. The autocatalytic acceleration of the decomposition of both solid and liquid phases by the products, the former of which may be neglected, since v_1 itself is small compared with v_2.

We may express the autocatalysis in the case of the molten part by writing v_2 in the form

$$v_2 = ax + b.$$

The total rate of decomposition will be

$$\frac{dx}{dt} = \underset{\text{Liquid phase.}}{f(x)v_2} + \underset{\text{Solid phase.}}{\left\{1 - f(x)\right\}v_1}.$$

$f(x)$, the amount of liquid phase introduced due to a quantit of decomposition product x, is found as follows. For small depres sions, Raoult's law will be obeyed and the lowering of the meltin point of tetryl by its decomposition products will be in accordanc with a straight-line law. The slope of the line is tan α (depressio of m. p. per unit amount of decomposition product). At a ten perature, θ, below the melting point T (= 129·1°) of the pure sul stance and above the eutectic temperature, the relative amoun of solid and liquid phases present are given by

$$\frac{\text{solid phase}}{\text{liquid phase}} = \frac{(T - \theta)\cot\alpha - x}{x}$$

For 1 gram of tetryl, and $\theta = 120{\cdot}0°$,

$$\text{Liquid phase, } f(x) = \frac{x}{(T - \theta)\cot\alpha}.$$

$$\text{Solid phase, } 1 - f(x) = 1 - \frac{x}{(T - \theta)\cot\alpha}.$$

Therefore

$$f(x) = \frac{x}{9{\cdot}1\cot\alpha}$$

and

$$\frac{dx}{dt} = \frac{x}{9{\cdot}1\cot\alpha}\cdot v_2 + \left\{1 - \frac{x}{9{\cdot}1\cot\alpha}\right\}v_1.$$

Putting $v_2 = ax + b$, and neglecting v_1x in comparison with $ax^2 + bx$, since v_1 is small compared with $ax + b$, we have

$$\left(\frac{dx}{dt} - v_1\right) = \frac{x}{9{\cdot}1 \cot \alpha}(ax + b).$$

Seven curves for different specimens of tetryl at 120° were analysed. These curves do not coincide with one another, since v_1 varies from one specimen to another, but $\left(\frac{dx}{dt} - v_1\right)$ plotted against x should give a single smooth curve for all specimens. Fig. 5 shows that this is so. The following are the results from which the curve is plotted; they refer to 5 grams of tetryl, and v_1 was obtained in the case of each of the seven specimens from its t_1x curve both by extrapolation and by taking the tangent at the origin.

	x.	$\left(\frac{dx}{dt} - v_1\right)$.		x.	$\left(\frac{dx}{dt} - v_1\right)$.
A	0·61	0·018	*D*	2·98	0·091
	2·0	0·050		7·08	0·221
	3·0	0·092			
	4·0	0·124			
	5·0	0·178	*E*	3·85	0·117
				7·00	0·218
B	2·0	0·046		9·70	0·366
	4·03	0·130			
	5·15	0·153			
	10·4	0·408	*F*	2·42	0·075
				5·59	0·170
				13·2	0·571
C	3·0	0·090			
	4·66	0·142	*G*	4·93	0·178
	7·52	0·252		13·6	0·616
	12·49	0·542			

The curves from which these are taken were very carefully plotted from the results of experiments in which the temperature did not vary by more than 0·1°.

The depression of the melting point of tetryl by its decomposition products was then measured.

Melting point after the evolution of 2·10 c.c. of gas per gram = 127·8°
,, ,, ,, 6·15 ,, ,, ,, = 125·2°
,, ,, ,, 11·2 ,, ,, ,, = 122·5°

Complete fusion occurred at 120° after the evolution of 15—16 c.c.; therefore,

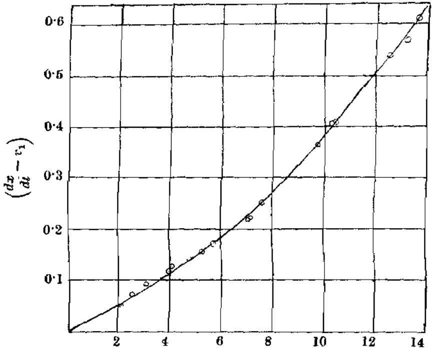
$$\tan \alpha = 0{\cdot}60 \text{ or } \cot \alpha = 1{\cdot}67$$

and

$$ax + b = \frac{9{\cdot}1 \times 1{\cdot}67 \left(\frac{dx}{dt} - v_1\right)}{x} \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

Thus $ax + b$, the rate of decomposition of *molten* tetryl at 120°, is connected with the acceleration in the decomposition of the

FIG. 5.



C.c. of gas evolved from 5 grams of tetryl at 120°.

solid. Dividing by 5 the values obtained from the curve in Fig. 5, to refer the results to 1 gram of tetryl instead of 5 grams, we obtain,

x.	$\left(\frac{dx}{dt} - v_1\right)$.
1·00	0·030
1·50	0·050
2·00	0·077
2·50	0·108

Substituting these results in equation (i) above, we find

$$ax + b = 0{\cdot}14x + 0{\cdot}30$$

and therefore for molten tetryl at 120° we have theoretically

$$\frac{dx}{dt} = 0{\cdot}14x + 0{\cdot}30;$$

hence,

$$t = \frac{1}{0{\cdot}14}\log_e\left(1 + \frac{0{\cdot}14}{0{\cdot}30}x\right)$$

$$= 16{\cdot}4 \log_{10}(1 + 0{\cdot}467x) \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

In order to compare values calculated from equation (ii) wit experimental results, 5 grams of tetryl were made molten at 12(

by adding other inert nitro-compounds. The agreement is shown in the following table.

Time in hours.	C.c. of gas from 5 grams of tetryl, calculated from equation (ii).	C.c. of gas from 5 grams of tetryl, rendered *molten by addition of* (*a*) dinitrobenzene.	(*b*) trinitrotoluene.		(*c*) trinitrotoluene and dinitrobenzene.
1	1·6	1·5	1·1	1·2	—
2	3·5	3·4	3·0	2·9	3·7
3	5·6	5·8	5·4	4·9	—
4	8·0	8·4	7·8	6·8	8·8
5	10·9	11·1	10·6	8·7	11·5
6	14·6	—	13·8	11·0	—

The agreement may be regarded as a quantitative proof that the acceleration is entirely due to the progressive production of liquid phase.

The question whether the variable quantity v_1—the initial rate of decomposition of the solid—depends largely on the residual impurity was discussed in the early part of this paper, and evidence was given to show that this is the case. A series of experiments on the repeated crystallisation of initially "pure" tetryl was made, and the values of v_1 after successive crystallisations under identical conditions were 0·025, 0·037, 0·024, 0·041, 0·021. It is well known, however, that impurities which dissolve in a solid substance, and the partition coefficient of which between the solid and the solvent is large, cannot be removed by crystallisation.

Summary.

The gradual decomposition of trinitrophenylmethylnitroamine (tetryl), which forms the basis of the standard stability test, is not so profound a change as that taking place when tetryl detonates. It satisfies the laws of a unimolecular, autocatalytic reaction.

The autocatalysis is due to the production of picric acid and in presence of added picric acid the reaction satisfies the equation established on this assumption.

Trinitrohydroxyphenylmethylnitroamine behaves similarly to tetryl. There is a large increase in the rate of decomposition when it melts. In the molten condition, its decomposition is catalysed by its own hydroxyl group as well as by picric acid. It catalyses the decomposition of tetryl to the same extent as picric acid. These relations suggest that this is an instance of hydrion catalysis in a substance in the fused state.

The acceleration in the initial stages of the decomposition of solid tetryl is connected quantitatively with the lowering of the melting point by the products of decomposition.

A comparison of the ratio of the velocities of decomposition of

solid and liquid tetryl at 120° with that deduced from the latent heat of fusion indicates that the decomposition of the solid is governed largely by traces of residual impurity which cannot be removed by recrystallisation.

This paper is published with the permission of the War Office. I have much pleasure in recording my indebtedness to Mr. Wm. Macnab for many kindnesses in connexion with this work.

DEPARTMENT OF EXPLOSIVES SUPPLY,
AND BALLIOL COLLEGE, OXFORD. [Received, March 14th, 1921.]

LXXVIII.—4-β-*Methylaminoethylglyoxaline.*

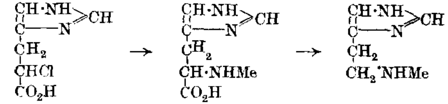
By ROBERT GEORGE FARGHER and FRANK LEE PYMAN.

THE isolation of 4-β-aminoethylglyoxaline from ergot, and the recognition of its importance as an intense stimulant of plain muscle, have led in recent years to the synthesis, not only of the substance itself, but also of a number of related compounds, the examination of which has indicated the presence of an optimum side-chain of two carbon atoms between the cyclic system and the amino-group (Ewins, T., 1911, **99**, 2052; Pyman, *ibid.*, 2172; 1916, **109**, 186). As the same optimum condition obtains in the sympathomimetic amines (Barger and Dale, *J. Physiol.*, 1910, **41**, 19), it was deemed of interest, in view of the importance of the *N*-alkyl substituent in that series, to prepare 4-β-*methylaminoethylglyoxaline* and to compare its physiological action with that of the naturally occurring base.

Considerable difficulty has been experienced in devising a practicable mode of preparation. The methods employed by Barger and his collaborators (Walpole, T., 1910, **97**, 941; Barger and Ewins, *ibid.*, 22, 53) for the synthesis of the analogously substituted β-phenylethylmethylamines were inapplicable, methylation of an acyl derivative of 4-β-aminoethylglyoxaline, for example, because of the readiness with which glyoxalines combine with alkyl esters, and syntheses dependent on 4-β-hydroxyethylglyoxaline or glyoxaline-4-acetaldehyde owing to the lack of satisfactory methods for the preparation of these substances.

Eventually, recourse was made to the preparation of dl-α-*methylamino-β-glyoxaline-4-propionic acid* (II) by the interaction of *dl*-α-chloro-β-glyoxaline-4-propionic acid (I) and 40 per cent.

aqueous methylamine at 110°, and the subsequent decarboxylation of this substance by means similar to those employed by Ewins and Pyman (T., 1911, **99**, 339) in the case of histidine.



(I.) (II.) (III.)

The yields of 4-β-*methylaminoethylglyoxaline* (III) were even poorer than had been anticipated, and the physiological action was disappointing, since the substance, when compared directly with 4-β-aminoethylglyoxaline, showed only about one-hundredth of the activity.

EXPERIMENTAL.

α-Chloro-β-glyoxaline-4-propionic Acid.

This acid has been prepared from histidine by Windaus and Vogt (*Beitr. Chem. Physiol. Path.*, 1908, **11**, 406) and by Gerngross (*Ber.*, 1909, **42**, 404), both of whom give the melting point as 191° (uncorr.). One of us (T., 1911, **99**, 1394) prepared the racemic variety of the acid synthetically, found that it melted at 201° (corr.), and concluded from the difference between the melting points that the acid prepared from histidine was one of the optically active varieties. Since we were in possession of considerable quantities of histidine, we desired to prepare α-chloro-β-glyoxaline-4-propionic acid from this source for the present investigation, as the synthesis involved a large number of operations. It appeared therefore to be desirable to examine the optical character of the product, a point which had received no attention from the previous investigators. We prepared the acid by the method of Windaus and Vogt, the crude product of the interaction of histidine, fuming hydrochloric acid, and sodium nitrite being esterified, and the ester purified by crystallisation of its hydrogen oxalate from methyl alcohol. Ethyl α-chloro-β-glyoxaline-4-propionate hydrogen oxalate, which was not analysed by the previous investigators, proves to be a *sesquioxalate.** It melts at 161—163° (corr.), and dissolves

* The formation of sesquioxalates in the place of the expected acid oxalates has been observed on several occasions amongst the derivatives of glyoxaline (T., 1911, **99**, 678, 1392, 1394). The hydrogen oxalate of ethyl β-glyoxaline-4-propionate is also a sesquioxalate (T., 1919, **115**, 1020) and not a normal acid oxalate containing a molecular proportion of water of crystallisation as stated by Windaus and Vogt (*Ber.*, 1907, **40**, 3693). Ethyl α-hydroxy-β-glyoxaline-4-propionate, however, yields a normal *hydrogen*

readily in water, but sparingly in cold methyl or ethyl alcohol. Late crops, melting as low as 140°, appear to represent the partly racemised salt, as the analytical figures remain unaltered [Found: C = 42·2; H = 4·7; Cl = 13·0. $(C_8H_{11}O_2N_2Cl)_4(C_2H_2O_4)_3$ requires C = 42·2; H = 4·7; Cl = 13·1 per cent.].

From this salt the ester was liberated and hydrolysed by the method of Windaus and Vogt, and the resulting α-chloro-β-glyoxaline-4-propionic acid purified by crystallisation from water. It proved to be optically inactive and identical with the synthetic acid. Either alone or mixed with the synthetic acid, it melted at 201° (corr.), although the melting point may be found as low as 195° when the acid is heated very slowly.

Racemisation of optically active amino-acids on the replacement of the amino-group by the chlorine atom has been observed on other occasions (compare, for instance, McKenzie and Clough, T., 1912, **101**, 391).

dl-α-*Methylamino-β-glyoxaline-4-propionic Acid* (dl-*Methylhistidine*).

Forty-four grams of α-chloro-β-glyoxaline-4-propionic acid and 176 c.c. of 40 per cent. aqueous methylamine (prepared by saturation in a freezing mixture) were heated in several sealed tubes for five hours at 110°. The resulting liquor was evaporated to dryness and the residue, after removal of methylamine as completely as possible by re-solution and re-evaporation, dissolved in water, and treated with a solution of 115 grams of picric acid in 3300 c.c. of water. On keeping, the liquor deposited first an oil, which was removed by filtration when the liquor was nearly cold, and then 52·3 grams of a well-crystallised picrate. This sintered at about 70° and melted at 132° and proved to be *α-methylamino-β-glyoxaline 4-propionic acid dipicrate*. By extracting the oil with hot water, some 35 grams of picrates melting indefinitely at about 70° were obtained, whilst the ultimate mother liquors yielded solely methylamine picrate melting at 210°. The picrates melting at 70° yielded after several crystallisations from water about 4 grams of methylhistidine dipicrate and 21 grams of a picrate melting at 189°, which proved to be *α-methylamino-β-glyoxaline-4-propionic acid sesquipicrate*, the ultimate mother liquors again depositing methylamine picrate. The total yield of methylhistidine is thus 47 per cent. of the theoretical.

---

oxalate, which separates from methyl alcohol, in which it is fairly readily soluble, in clusters of prismatic needles which are anhydrous and melt at 143° (*corr.*), *sintering from* 135° (*Found*: C = 43·6; H = 5·3; N = 10·2. $C_8H_{12}O_3N_2,C_2H_2O_4$ requires C = 43·8; H = 5·2; N = 10·2 per cent.).

When less concentrated solutions of methylamine were employed, the yield of methylhistidine was diminished; thus, when a 29 per cent. solution of methylamine was used, the yield of methylhistidine amounted to only 20 per cent. of the theoretical.

α-Methylamino-β-glyoxaline-4-propionic acid dipicrate crystallises from water in well-defined, prismatic needles containing 3 molecules of water of crystallisation, two of which are lost at 60° in a vacuum, and the third slowly at 90° in a vacuum. The air-dried picrate sinters at about 70°, owing to loss of water of crystallisation, and melts definitely at 132° (corr.). It dissolves readily in boiling water but only sparingly in cold (Found: in air-dried material, loss at 60° in a vacuum = 5·4. $C_7H_{11}O_2N_3,2C_6H_3O_7N_3,3H_2O$ requires loss of $2H_2O$, 5·3 per cent. Found: in dried material, C = 35·3; H = 3·3; N = 19·3; further loss at 90° in a vacuum = 2·8. $C_7H_{11}O_2N_3,2C_6H_3O_7N_3,H_2O$ requires C = 35·3; H = 3·0; N = 19·5; H_2O = 2·6 per cent.).

Five grams of air-dried picrate gave 3·32 grams of picric acid, 3·36 grams being required.

α-Methylamino-β-glyoxaline-4-propionic acid sesquipicrate, which closely resembles the dipicrate, crystallises from water in large, glistening, rhombic prisms, which melt at 193° (corr.) and appear to contain 7 molecules of water of crystallisation, of which six are lost at 60° in a vacuum, whilst the last is retained even on further heating at 110° (Found: in air-dried material, loss at 60° in a vacuum = 9·6, 9·4; C = 33·1; H = 3·7.

$$2C_7H_{11}O_2N_3,3C_6H_3O_7N_3,7H_2O$$

requires loss of $6H_2O$ = 9·4; C = 33·35; H = 3·9 per cent.

Found: in dried material, C = 36·8; H = 3·2; N = 20·0.

$$2C_7H_{11}O_2N_3,3C_6H_3O_7N_3,H_2O$$

requires C = 36·8; H = 3·2; N = 20·1 per cent.).

α-Methylamino-β-glyoxaline-4-propionic acid monopicrate was obtained by treating the solution of the base with a molecular proportion of picric acid. It is sparingly soluble in water, from which it separates in minute, flattened prisms, which melt and effervesce at 118° (corr.) and contain 3 molecules of water of crystallisation, which are not lost on heating at 60° in a vacuum (Found: C = 34·7; H = 4·3. $C_7H_{11}O_2N_3,C_6H_3O_7N_3,3H_2O$ requires C = 34·5; H = 4·45 per cent.).

α-Methylamino-β-glyoxaline-4-propionic acid dihydrochloride was prepared from the picrate in the usual manner and crystallised from dilute hydrochloric acid in large, diamond-shaped, colourless plates, which softened at about 127° and melted at 134° (corr.). It dissolves very readily in water, but only sparingly in alcohol. The air-dried salt contains one molecule of water of crystallisation,

which is not lost on heating at 60° in a vacuum. The solution in sodium carbonate gives a blood-red colour with sodium diazobenzene-*p*-sulphonate (Found : loss in a vacuum at 60° = 1·2 per cent. In dried material, C = 32·5; H = 5·6; N = 15·9; Cl = 26·9. $C_7H_{11}O_2N_3,2HCl,H_2O$ *requires* C = 32·3; H = 5·8; N = 16·1; Cl = 27·3 per cent.).

α-Methylamino-β-glyoxaline-4-propionic acid aurichloride separates from water, in which it is only sparingly soluble, in glistening, pale orange, flattened prisms, which are anhydrous and effervesce at 115° (corr.) without melting (Found : Au = 46·7.

$$C_7H_{11}O_2N_3,2HCl,2AuCl_3$$

requires Au = 46·4 per cent.).

α-Methylamino-β-glyoxaline-4-propionic acid is prepared by digesting an aqueous solution of the hydrochloride with slightly more than the quantity of silver carbonate calculated to remove the hydrochloric acid completely. It separates from the resulting solution, after concentration, in needles, which melt and effervesce at 270° (corr.), are anhydrous, and taste sweet with a bitter aftertaste (Loss at 110° = 1·3 per cent. Found: in dried material, C = 49·5; H = 6·5; N = 24·5. $C_7H_{11}O_2N_3$ *requires* C = 49·7; H = 6·6; N = 24·8 per cent.).

The *benzoyl* derivative, obtained by the Schotten-Baumann method, separates from water, in which it is much more readily soluble than the corresponding histidine derivative, in clusters of minute prisms, which give an intense red coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution. The air-dried material retains one-half of a molecular proportion of water of crystallisation, which is lost at 110°. It melts and effervesces at 241° (corr.) [Found : in air-dried material, C = 59·5; H = 5·6; loss at 110° = 2·9. $(C_{14}H_{15}O_3N_3)_2,H_2O$ requires C = 59·5; H = 5·7; H_2O = 3·2 per cent.].

4-β-*Methylaminoethylglyoxaline.*

This base can be prepared in poor yield by the decarboxylation of the preceding benzoyl derivative and hydrolysis of the product or by decarboxylation of methylhistidine by means of 20 per cent. hydrochloric acid at 280°. Unlike the parent base (compare Ewins and Pyman, *loc. cit.*), it cannot be prepared by the action of 20 per cent. sulphuric acid on methylhistidine, the reaction resulting in almost complete decomposition of the methylhistidine and reduction of the sulphuric acid to hydrogen sulphide at temperatures of 270—290°, whilst below 270° little decarboxylation occurs.

(*a*) *Formation of 4-β-Methylaminoethylglyoxaline from Benzoylmethylhistidine.*—1·2 Grams of benzoylmethylhistidine were heated

at 240° in a vacuum until all frothing ceased. The dark residue was dissolved in 4 c.c. of 20 per cent. hydrochloric acid, heated for one hour at 180°, and the resulting solution freed from benzoic acid by extraction with ether, basified with sodium carbonate, filtered from insoluble brown matter, acidified to methyl-orange, evaporated to dryness, and extracted with alcohol. The extract, which consisted in part of sodium chloride, was dissolved in a little water and treated with 0·5 gram of picric acid in 12 c.c. of water. After the separation of resinous matter, 0·25 gram of nearly pure 4-β-methylaminoethylglyoxaline dipicrate was obtained. The yield amounts to 10 per cent. of the theoretical.

(*b*) *Formation of 4-β-Methylaminoethylglyoxaline from Methylhistidine*.—4·5 Grams of methylhistidine dihydrochloride dissolved in 18 c.c. of 20 per cent. hydrochloric acid were heated in nine sealed tubes for two hours at 280°. The product was basified with sodium carbonate, filtered from insoluble amorphous matter, re-acidified to methyl-orange, evaporated to dryness, and extracted with alcohol. The residue consisted solely of sodium chloride. The extracted material, amounting to 2·5 grams, and consisting in part of sodium chloride, was dissolved in a little water and treated with a hot solution of 3 grams of picric acid in 75 c.c. of water. After the deposition of resinous matter and amorphous picrates, there crystallised 1·0 gram of nearly pure 4-β-methylaminoethylglyoxaline dipicrate, which sintered at 170° and melted and decomposed at about 210°. The mother liquors were used to re-extract the amorphous picrates and yielded altogether a further 0·3 gram of the crystalline dipicrate. The yield thus amounts to 12 per cent. of the theoretical.

4-β-*Methylaminoethylglyoxaline dipicrate* crystallises from water, in which it is sparingly soluble, in well-defined, bright yellow needles, which appear to contain 2 molecules of water of crystallisation, one of which is lost on heating at 60° in a vacuum. The air-dried product shrinks together at about 170°, doubtless owing to loss of water of crystallisation, and melts and decomposes at 220° (corr.) (Found: loss at 60° in a vacuum = 3·6. $C_6H_{11}N_3,2C_6H_3O_7N_3,2H_2O$ requires loss of $1H_2O$ = 2·9 per cent.

Found: in material dried at 60° in a vacuum, C = 36·0; H = 3·2. $C_6H_{11}N_3,2C_6H_3O_7N_3,H_2O$ requires C = 35·9; H = 3·2 per cent.).

4-β-*Methylaminoethylglyoxaline dihydrobromide*, prepared from the picrate in the normal manner, was obtained on evaporation of the aqueous solution as a somewhat hygroscopic, crystalline powder. It separates from alcohol in fern-shaped clusters of needles, which melt at 275° (corr.) and contain $2H_2O$. It is very readily soluble in water, readily soluble in alcohol, but almost insoluble in ether

or ethyl acetate. The solution in sodium carbonate gives a blood-red colour with sodium diazobenzene-*p*-sulphonate (Found: loss at 60° in a vacuum = 2·4 per cent. Found: in dried material, C = 22·4; H = 4·9; N = 12·8. $C_6H_{11}N_3,2HBr,2H_2O$ requires C = 22·3; H = 5·3; N = 13·0 per cent.).

In conclusion, the authors would express their indebtedness to Dr. H. H. Dale, F.R.S., of the staff of the Medical Research Committee, who has carried out the experiments on the physiological action of 4-β-methylaminoethylglyoxaline.

WELLCOME CHEMICAL RESEARCH LABORATORIES.

[*Received, April 13th*, 1921.]

LXXIX.—*Physical and Physiological Properties of some Hydrogenated Quinoline Compounds.*

By AKIRA SHIMOMURA and JULIUS BEREND COHEN.

IT has been shown by Bamberger and his co-workers (*Ber.*, 1890, **23**, 1138; 1891, **24**, 2463; *Annalen*, 1890, **257**, 1) that a hydrogenated quinoline compound acquires the nature of an alkylated aromatic amine, and the results of the experiments carried out by them led them to adopt a centric formula for naphthalene, quinoline, and similar condensed nuclei.

The present experiments were carried out in the hope of finding if there exists any relation between a hydrogenated quinoline compound and the corresponding aromatic amine in regard to their ultra-violet absorption spectra.

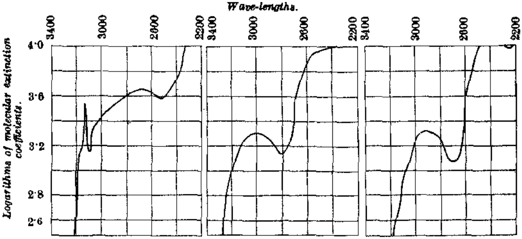
The following compounds were spectrographically examined:

Quinoline compounds.	Aromatic amines.
Quinoline (in alcohol).	
1 : 2 : 3 : 4-Tetrahydroquinoline (in alcohol).	Monomethyl-*o*-toluidine (in alcohol).
6-Amino-1 : 2 : 3 : 4-tetrahydroquinoline dihydrochloride (in water).	2 : 5-Tolylenediamine dihydrochloride (in water).
α-Naphthaquinoline (in alcohol).	
1 : 2 : 3 : 4-Tetrahydro-α-naphthaquinoline (in alcohol).	
1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-Octahydro-α-naphthaquinoline (in alcohol).	
β-Naphthaquinoline (in alcohol).	
1 : 2 : 3 : 4-Tetrahydro-β-naphthaquinoline (in alcohol).	1-Methyl-2-naphthylamine (in alcohol).
1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-Octahydro-β-naphthaquinoline (in alcohol).	

From the spectrographic results, the following generalisation can be drawn :

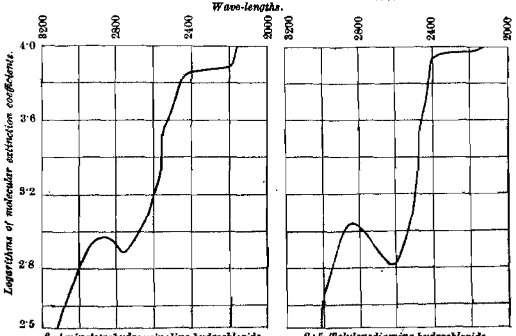
(1) A hydrogenated quinoline compound shows quite a different absorption from that of the original compound, due to the change of structure of the molecule.

FIG. 1. FIG. 2. FIG. 3.



Quinoline. *Tetrahydroquinoline.* *Monomethyl-o-toluidine.*

FIG. 4. FIG. 5.



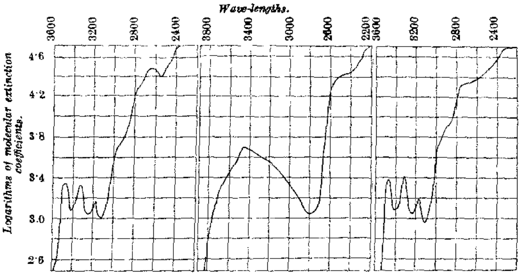
6-Aminotetrahydroquinoline hydrochloride. *2:5-Tolylenediamine hydrochloride.*

(2) The absorption curve shown by a hydrogenated quinoline compound is very similar in its general form to that of the corresponding alkylated aromatic amine. Hence the resemblance of these two series of compounds is proved spectrographically as well as chemically.

(3) As the degree of hydrogenation increases in a quinoline compound, the tendency to exhibit distinct absorption bands decreases.

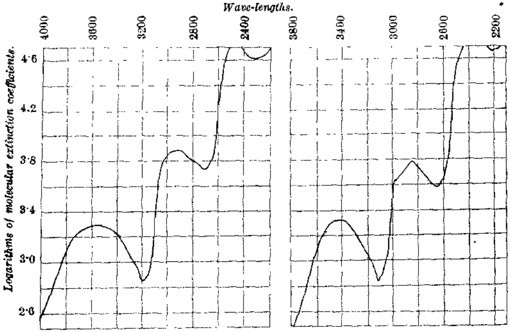
(4) A quinoline compound of a higher molecular weight shows more bands than one of a lower molecular weight.

FIG. 6. FIG. 7. FIG. 9.



α-Naphthaquinoline. Tetrahydro-α-naphthaquinoline. β-Naphthaquinoline.

FIG. 10. FIG. 11.



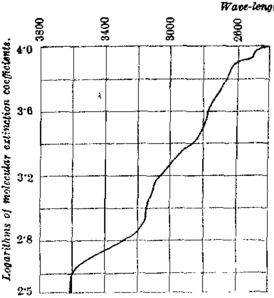
Tetrahydro-β-naphthaquinoline. 1-Methyl-2-naphthylamine.

(5) Although α- and β-naphthaquinolines show rather similar absorption, that of their tetrahydro-derivatives is entirely different.

Judging from the results obtained above, it might be safely predicted that a compound having a structure

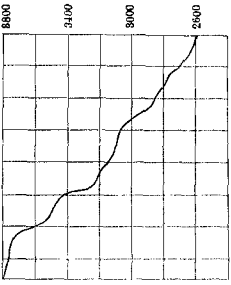
will

FIG. 8.



ar-*Octahydro-α-naphthaquinoline.*

FIG. 12.



ar-*Octahydro-β-naphthaquinoline.*

show an absorption curve similar to that of tetrahydro-α-naphthaquinoline, *and so on.*

The antiseptic properties of some of these quinoline compounds were examined by Prof. C. H. Browning of Glasgow University, with the following results :

Compound.	*Staphylococcus pyogenes aureus* in peptone water.	*Staphylococcus pyogenes aureus* in serum.	*Bacillus coli* in peptone water.	*Bacillus coli* in serum.
Quinoline *hydrochloride.*	1 : 4000 + *1 : 2000 —*	1 : 1000 + ? —	1 : 2000 + *1 : 1000 —*	1 : 1000 + ? —
Tetrahydro-quinoline hydrochloride.	1 : 2000 + 1 : 1000 —	1 : 1000 + ? —	1 : 1000 + ? —	1 : 1000 + ? —
Methyltetra-hydroquinoline methiodide.	1 : 1000 + ? —	1 : 1000 + (some ppt.) ? —	1 : 1000 + ? —	1 : 1000 + ? —
α-Naphtha-quinoline hydrochloride.	1 10,000 + *1 : 4000 —*	1 : 2000 + *1 : 1000 inhib.*	1 : 2000 + (ppt.) *1 : 1000 — (ppt.)*	1 : 1000 + ? —
Tetrahydro-α-naphtha-quinoline hydrochloride.	1 : 10,000 + 1 : 4000 — (ppt.)	1 : 1000 + ? —	1 : 10,000 + (ppt.) *1 : 4000 — (ppt.)*	1 : 1000 + ? —
β-Naphtha-quinoline hydrochloride.	1 : 10,000 + 1 : 4000 — (ppt.)	1 : 2000 + 1 : 1000 inhib.	1 : 10,000 + 1 : 4000 — (ppt.)	1 : 1000 + ? —
Tetrahydro-β-naphtha-quinoline hydrochloride.	1 : 10,000 + 1 : 2000 — (ppt.)	1 : 2000 + 1 : 1000 inhib.	1 : 4000 + (ppt.) 1 : 2000 — (ppt.)	1 : 1000 + ? —

+ = Vigorous growth. inhib. = Inhibition of growth.
— = Sterility after twenty-four to forty-eight hours.

Experimental.

Tetrahydroquinoline.

Quinoline was reduced with tin and hydrochloric acid according to Hoffmann's method (*Ber.*, 1883, **16**, 728). The crude tetrahydroquinoline, containing some unchanged quinoline, was warmed with concentrated hydrochloric acid on a water-bath until crystals of the hydrochloride appeared. The hydrochloride was pressed on a porous plate and washed with a little hot benzene, and then recrystallised from alcohol. The hydrochloride, consisting of colourless, slender needles, melted at 180—181°.

The free base was obtained from its hydrochloride as an almost colourless oil, boiling at 160°/72 mm.

6-Aminotetrahydroquinoline.

This compound was prepared according to Bamberger (*Annalen*, 1890, **257**, 24) by combining tetrahydroquinoline hydrochloride with diazotised sulphanilic acid and subsequently reducing the azo-compound with stannous chloride.

The free base crystallises from benzene in colourless leaflets, m. p. 97°, and is extremely oxidisable, changing slowly into a black mass. It was kept in the form of the hydrochloride (m. p. 243°), which was quite stable.

Methyltetrahydroquinoline methiodide.

Tetrahydroquinoline, obtained from 2 grams of the hydrochloride, was mixed with 14 grams of freshly distilled methyl iodide, whereby oily drops soon appeared, which gradually solidified to a crystalline mass (Hoffmann and Königs, *Ber.*, 1883, **16**, 732; Wedekind, *Ber.*, 1902, **35**, 773). It was warmed on the water-bath for one hour and left to stand overnight. After an excess of methyl iodide had been driven off, the residue was dissolved in water, made alkaline with ammonia, and the separated oil extracted with ether. The aqueous solution, thus freed from any kairoline, was evaporated nearly to dryness on the water-bath, and the residue dissolved in hot alcohol and precipitated by careful addition of ether. This procedure was repeated several times to obtain the methiodide in colourless needles, which melted at about 172° with decomposition.

Monomethyl-o-toluidine.

Crude monomethyl-*o*-toluidine was prepared by heating 23 grams of *o*-toluidine, 12·3 grams of methyl alcohol (acetone-free) and 21·5 grams of concentrated hydrochloric acid in a sealed tube

at 200—220° for eight hours (Nölting, *Ber.*, 1878, **11**, 2278). It was converted into its nitroso-compound, and by subsequent reduction by stannous chloride the pure monomethyl compound was obtained as a colourless oil, when freshly distilled; but it soon oxidised and became discoloured. It boiled at 206—208°.

2 : 5-*Tolylenediamine.*

5-*Nitro*-o-*toluidine* (Beilstein and Kuhlberg, *Annalen*, 1871, **158**, 348, 352).—Eight grams of powdered aceto-*o*-toluidide were added little by little to 28 grams of fuming nitric acid which had been previously cooled by a freezing mixture. Nitration was carried out at about − 5°. The mixture was left to stand overnight, then poured into a large bulk of cold water, whereby the nitro-product separated as a yellow precipitate, which was subsequently hydrolysed with boiling dilute sulphuric acid (30 grams of concentrated acid in 90 c.c. of water). After all had been hydrolysed, it was subjected to steam distillation (Cohen and Dakin, T., 1901, **79**, 1127), in the course of which a small amount of 3-nitro-*o*-toluidine distilled with water as fine, orange-yellow needles (m. p. 92—97°). The residue in the flask was made alkaline with ammonia, and the 5-nitro-*o*-toluidine separated and purified by recrystallisation from a large bulk of hot water. It was obtained in lemon-yellow needles, m. p. 134—135°.

2 : 5-*Tolylenediamine.*—5-Nitro-*o*-toluidine was easily reduced by granulated tin and concentrated hydrochloric acid. Colourless plates of the tin double salt of the base separated from the cooled filtrate, which were dissolved in water and decomposed by hydrogen sulphide. Slightly greyish-white hydrochloride of 2 : 5-tolylenediamine was obtained by evaporating the filtrate from tin sulphide. The free base is very unstable.

1 : 2 : 3 : 4-*Tetrahydro-α-naphthaquinoline.*

Tetrahydro-α-naphthaquinoline was prepared according to Bamberger's method (*Ber.*, 1891, **24**, 2475) by reducing α-naphthaquinoline with tin and hydrochloric acid.

The hydrochloride, which crystallises from alcohol in thick, colourless prisms, melts at 260° with decomposition. The free base melts at about 45°.

1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*Octahydro-α-naphthaquinoline.*

α-Naphthaquinoline was reduced with metallic sodium and boiling amyl alcohol according to the method of Bamberger and Stettenheimer (*Ber.*, 1891, **24**, 2488).

The base was purified by distillation in a vacuum, and boiled at 192—193°/8—10 mm.

1 : 2 : 3 : 4-*Tetrahydro*-β-*naphthaquinoline.*

This compound was obtained in the same way as the α-compound, by reducing β-naphthaquinoline with tin and hydrochloric acid (Bamberger and Müller, *Ber.*, 1891, **24**, 2643).

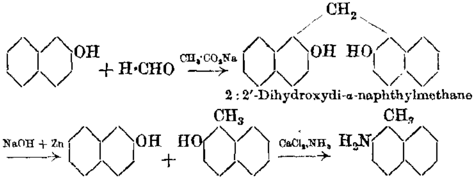
The hydrochloride crystallises from hydrochloric acid in colourless leaflets, which shrink and then melt at 231°.

1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*Octahydro*-β-*naphthaquinoline.*

β-Naphthaquinoline was treated like the α-compound with sodium and amyl alcohol (Bamberger and Müller, *Ber.*, 1891, **24**, 2658). A trace of *ac*-octahydro-compound was precipitated as carbonate by passing a current of carbon dioxide through the ethereal solution of the reduced products. The base was purified by distillation under reduced pressure.

1-*Methyl*-2-*naphthylamine.*

This compound was prepared according to the method of Fries and Hübner (*Ber.*, 1906, **39**, 439). The scheme of reactions is as follows :



2 : 2′-Dihydroxydi-α-naphthylmethane crystallises from glacial acetic acid in a felted mass of colourless needles, m. p. 199·5—200°.

1-Methyl-2-naphthol crystallises from hot water in colourless fibrous needles, m. p. 110°.

1-*Methyl*-2-*naphthylamine.*—In order to replace the hydroxyl group of 1-methyl-2-naphthol by the amino-group, Bucherer's method of conversion of β-naphthol into β-naphthylamine was tried (*J. pr. Chem.*, 1904, [ii], **69**, 88), that is, heating 3 grams of 1-methyl-2-naphthol with a mixture of 5 c.c. of 40 per cent. solution of ammonium sulphite and 5 c.c. of concentrated ammonia in a sealed tube at 150—160° for seven hours. But no change was

found to have taken place, due probably to the steric hindrance of the methyl group in the ortho-position to the hydroxy-group.

Amination, however, can be brought about by heating the naphthol with four times its weight of calcium chloride-ammonia in a sealed tube at 270° for eight hours.

1-Methyl-2-naphthylamine crystallises from light petroleum in thick, colourless prisms, m. p. 50—51°.

Spectrography.

The experiments were carried out by using Adam Hilger's rotating sector spectrophotometric attachment, the spark from a nickel–iron alloy being employed as a source of light.

The absorption curves are drawn on wave-lengths against logarithms of molecular extinction coefficients, $\log\left(\frac{I_0}{I}\right) \div dc$, where I_0 and I are the intensities of the incident and emergent light respectively, d the thickness of the absorbing layer, and c the molecular concentration.

The authors take this opportunity to express their hearty thanks to Prof. E. C. C. Baly, of Liverpool University, for his kindness in placing his spectrophotometer at their service.

THE ORGANIC CHEMICAL LABORATORIES,
THE UNIVERSITY, LEEDS. [*Received, March 18th*, 1921.]

LXXX.—*Interaction of Acetylene and Mercuric Chloride. Part II.*

By WILLIAM JOB JENKINS.

IN a former communication by Chapman and Jenkins (T., 1919, **115**, 847) an account was given of a new method of preparing Biginelli's additive compound of mercuric chloride and acetylene (Biginelli, *Ann. Farm. Chem.*, 1898, 16; Brame, T., 1905, **87**, 427), to which the constitutional formula ClHg·HC:CHCl has been assigned. It has since been found that the yield of this compound obtained by the method therein described can be considerably improved if purified acetylene * is used in the preparation. Further-

* The purification of acetylene from those contaminating gases, which would interact with mercuric chloride or its additive compound with acetylene, was found to be most conveniently effected by passing the impure gas through a heated glass tube packed loosely with slaked lime. The acetylene purified in this way had entirely lost its unpleasant odour.

more, the compound made from purified acetylene is much more stable than that obtained from the impure gas, and does not exhibit signs of melting, when quickly heated, until its temperature has been raised to 129°.

From the constitution assigned to Biginelli's compound, it seemed reasonable to conclude that other additive compounds of mercuric chloride and acetylene should be capable of existence. Thus two molecules of acetylene might unite with one molecule of mercuric chloride to form a compound having the formula $CHCl{:}CH{\cdot}Hg{\cdot}CH{:}CHCl$ (I), or one molecule of acetylene might unite with two molecules of mercuric chloride to form a saturated compound with the constitutional formula $(ClHg)_2CH{\cdot}CHCl_2$ (II).

My efforts to obtain either of these two compounds by direct combination of acetylene and mercuric chloride have been futile. I have, however, succeeded in preparing compound (I) by an indirect method, namely, the removal of one molecule of mercuric chloride from Biginelli's compound. Up to the present I have been able to discover only one reagent—ammonia—by means of which this removal of mercuric chloride could be effected, the action being represented by the equation

$$2NH_3 + 2CHCl{:}CH{\cdot}HgCl = CHCl{:}CH{\cdot}Hg{\cdot}CH{:}CHCl + Hg(NH_3Cl)_2.$$

I have not, as yet, succeeded in preparing the saturated compound.

When dry ammonia was bubbled through a solution of the compound $HgCl_2,C_2H_2$ in dry chloroform, a white precipitate was formed immediately, but more than an hour was required to complete the precipitation. There was no evidence that acetylene was liberated during the reaction. On heating, the white precipitate fused, with evolution of ammonia, and sublimed as mercuric chloride.

The analysis of the substance (Found: C = 1·09; H = 2·05; Cl = 20·57; NH_3 = 10·60; Hg = 64·80 per cent.), and its properties, prove that it is rather impure fusible white precipitate.

From the filtrate, after concentration, white crystals separated (Found: C = 13·99, 14·30; H = 1·27, 1·23; Cl = 21·11; Hg = 62·02. $HgCl_2,2C_2H_2$ requires C = 14·84; H = 1·24; Cl = 21·98; Hg = 61·94 per cent.).

This new additive *compound* is a well-defined, crystalline substance, m. p. 60°, very soluble in ether, chloroform, or benzene. It can also be prepared together with fusible white precipitate by passing ammonia into a solution of the compound $HgCl_2,C_2H_2$ in benzene. When a concentrated solution of the new compound in chloroform or benzene was heated for some time, acetylene was slowly evolved and crystals of Biginelli's compound separated.

Formula (I) appears to represent satisfactorily the properties of the new additive compound, so far as these are at present known.

It will be observed that the formulæ assigned to Biginelli's compound and the new compound represent them as being similarly constituted to the mercury alkyl haloids and the mercury dialkyls respectively, and, accordingly, account for the circumstance that the melting point of the new compound is 70° lower than that of Biginelli's compound.

The above work was carried out at the Sir Leoline Jenkins Laboratories, Jesus College, Oxford, and I wish to record my thanks to Mr. Chapman, F.R.S., for his advice and help.

THE CHEMICAL DEPARTMENT,
UNIVERSITY OF BRISTOL. [*Received, April 9th, 1921.*]

LXXXI.—*The Catalytic Oxidation of Ferrous Salts in Acid Solutions.*

By RICHARD THOMAS and EDWARD THOMAS WILLIAMS.

FERROUS salts are reputed to be easily oxidised on exposure to air, and text-books of analytical chemistry prescribe elaborate precautions for the exclusion of air in making up standard solutions of these salts. In point of fact, acid solutions of ferrous salts are not easily oxidised, even in the presence of certain well-known oxygen carriers such as compounds of manganese, cobalt, etc. Baskerville and Stevenson (*J. Amer. Chem. Soc.*, 1911, **33**, 1105) have shown that there is no detectable oxidation of a solution of ferrous ammonium sulphate acidified with sulphuric acid through which air or oxygen has been passed for several hours. Similar results were obtained with ferrous sulphate, and these authors conclude that at the ordinary temperature in acid and neutral solutions, the ferrous ion is so slowly oxidised, and the oxidation so slightly affected by such substances as are apt to be present, that in ordinary estimations of iron by titration with potassium permanganate, expulsion of air during reduction by zinc is unnecessary, and the titration may be performed at leisure.

Ennos (*Proc. Camb. Phil. Soc.*, 1913, **17**, 182) passed air at the rate of 1 litre every three hours through 0·1*N*-solution of ferrous sulphate at 25° and found that 0·03 per cent. of the sulphate was oxidised after one hour. He also found that this rate is doubled with a

rise of temperature of 10°, and that at 60° the rate of oxidation of the chloride is only about one-tenth that of the sulphate. Ennos further states that the reaction is of the second order as regards ferrous sulphate, and is proportional to the partial pressure of oxygen. He regards the oxidation as depending on the non-ionised molecules of the ferrous salt.

As already mentioned in the preceding paragraph, most of the usual well-known oxygen carriers have comparatively little catalytic effect on the oxidation of ferrous salts in acid and neutral solutions. The action of oxides of nitrogen as catalysts for this reaction appears to be specific. McCulloch (Eng. Pat. 17112, 1894) described a process for oxidising ferrous compounds to ferric compounds in acid solution by means of air, using nitric oxide as an oxygen carrier. A dynamical study of the catalytic effect produced by nitric oxide or nitrogen trioxide affords some interesting side-lights on catalysis generally, and the present communication embodies some of the results obtained.

EXPERIMENTAL.

The apparatus employed for studying the catalytic oxidation of ferrous salts by oxygen in the presence of nitric oxide was substantially the same as one already used by one of us (Thomas, *J. Soc. Chem. Ind.*, 1920, **39**, 10T) for investigating the addition of hydrogen to unsaturated glycerides in the presence of nickel as catalyst. Solutions of ferrous chloride with hydrochloric acid and the catalyst were shaken with oxygen, and the rate of absorption of the latter at atmospheric pressure was measured. The nitric oxide was conveniently added in the form of sodium nitrite, which furnishes the oxide immediately with the ferrous salt and hydrochloric acid.

The effects of temperature, concentration of ferrous chloride, and concentration of nitric oxide on the rate of reaction were determined with the following results. It was found that under all conditions the rate of absorption of oxygen was inversely proportional to the concentration of ferrous chloride, so that the oxidation proceeds with an acceleration, in spite of the fact that the active mass of the substance undergoing oxidation is decreasing. This is at first sight suggestive of autocatalysis by the ferric chloride produced. Such is not the case, however, as can easily be shown by constructing velocity equations on this assumption. Further, it is negatived by the fact that the foregoing result holds good for varying initial concentrations of ferrous chloride; the rate at which oxygen is absorbed is doubled when the initial concentration of

ferrous chloride is halved, which would naturally not be the case if we are dealing with autocatalysis brought about by the product of oxidation. Finally, the suggestion is contrary to the fact that the initial addition of ferric chloride produces no increased rate of absorption. We must therefore seek elsewhere for an explanation of the retarding effect of ferrous salt concentration on its rate of oxidation. The significance of this result will he discussed later.

If a is the initial concentration of ferrous chloride, and an amount x has been transformed to ferric chloride after an interval of time t, then if the rate of the reaction is inversely proportional to the concentration of ferrous salt, the velocity equations will be as follows:

$$\frac{dx}{dt} = \frac{k}{a - x}$$

which on integration gives

$$x(a - \frac{x}{2}) = kt \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$

The values of k in the tables given below are derived from equation (i).

TABLE I.

Twelve grams of ferrous chloride tetrahydrate, 2·2 grams of hydrochloric acid, and 0·12 gram of sodium nitrite were made up to a total volume of 35 c.c. with water. The hydrochloric acid is just sufficient in amount to prevent the formation of basic ferric chloride and the quantity of sodium nitrite is 1·56 per cent. of that of the ferrous chloride. Temperature 20°.

	a.		b.	
Time in minutes.	C.c. of oxygen absorbed.	k.	C.c. of oxygen absorbed.	k.
4	50	4180	48	4032
6	76	4079	75	4037
8	104	4004	100	3875
10	132	3882	—	—
12	163	3800	160	3733
14	200	3720	203	3741
16	250	3730	—	—
18	—	—	299	3500
20	350	—	349	—

The total possible oxygen absorption is 360 c.c. at 16°. This is the value of a in equation (i), and x is obtained from the second column.

Influence of Initial Concentration of Ferrous Chloride.

Table II shows the effect of the initial concentration of ferrous chloride on the velocity of absorption of oxygen. The amount of

sodium nitrite is the same as in Table I, whilst the quantity of hydrochloric acid is varied in the same proportion as the ferrous salt.

TABLE II.

Temperature 20°.

a. 6 Grams of $FeCl_2,4H_2O$. Time in minutes.	C.c. of oxygen absorbed.	*k.*	*b.* 15 Grams of $FeCl_2,4H_2O$. Time in minutes.	C.c. of oxygen absorbed.	*k.*
1	23	3887	4	35	3780
2	50	3875	8	74	3820
3	81	3780	12	116	3789
4	126	3686	16	158	3670
5	175	—	20	210	3623
			26	300	3500
			32	426	—

The total possible oxygen absorption is 180 c.c. in the first case and 450 c.c. in the second.

It will be seen from the above figures that the time required for a given oxygen absorption is proportional to the initial concentration of ferrous chloride. The velocity equation having been deduced on the assumption that the rate of absorption is *inversely proportional to the ferrous salt concentration, k*—the velocity of the reaction at unit concentration—remains constant.

Influence of Concentration of the Catalyst.

The effect of the concentration of the catalyst (nitric oxide) on the rate of oxidation of ferrous chloride was next investigated. The quantities of ferrous chloride tetrahydrate were as in Table I, whilst 0·06 gram (*a*), 0·12 gram (*b*), and 0·24 gram (*c*) of sodium nitrite were used respectively.

TABLE III.

a. Time in minutes.	C.c. of oxygen absorbed.	*k.*	*b.* Time in minutes.	C.c. of oxygen absorbed.	*k.*	*c.* Time in minutes.	C.c. of oxygen absorbed.	*k.*
6	30	1725	4	48	4032	2	58	9399
15	80	1706	6	75	4037	3	90	9450
21	109	1600	8	100	3875	4	130	9588
24	130	1600	12	160	3733	5	172	9430
30	170	1560	14	203	3741	6	225	9300
			16	250	3680	7	300	(9000)
			20	349	—	8	338	—

By increasing the amount of sodium nitrite from 0·06 gram to 0·12 gram the rate of absorption of oxygen is increased 2·4 times, whilst when the amount is increased from 0·12 gram to 0·24 gram,

the velocity is increased 2·3 times. Thus the rate of reaction is approximately proportional to the concentration of the catalyst.

Influence of Temperature.

The quantities of the various substances were as in Table I, and the temperature was 30°.

TABLE IV.

Time in minutes.	C.c. of oxygen absorbed.	k.	Time in minutes.	C.c. of oxygen absorbed.	k.
2	40	6800	6	137	6666
3	62	6820	8	200	6500
4	86	6815	10	275	(6133)
5	112	6809	12	346	

An increase of temperature of 10° brings about a 1·8-fold increase in velocity.

Effect of Hydrochloric Acid.

The following results show that hydrochloric acid has no effect on the velocity of the reaction. In the first case there is enough acid to prevent entirely the formation of any basic ferric chloride, namely, 2·2 grams for 12 grams of the tetrahydrate. In the second case the quantity of acid was reduced to 0·22 gram, which is but little more than the amount necessary to decompose the sodium nitrite (0·12 gram).

TABLE V.

2·2 Grams of hydrochloric acid.			0·22 Gram of hydrochloric acid.		
Time in minutes.	C.c. of oxygen absorbed.	k.	Time in minutes.	C.c. of oxygen absorbed.	k.
4	50	4180	2	24	4176
6	76	4079	5	64	4160
8	104	4004	7	94	4196
10	132	3882	10	142	4103
12	163	3800	12	177	4012
14	200	3720	15	250	3920
16	250	3730	17	332	—
20	350	—			

Thus k is independent of the concentration of the hydrochloric acid.

Discussion of Results in Relation to Theories of Catalysis.

The experiments described above have shown that the rate of absorption of oxygen is proportional to the concentration of the catalyst, inversely proportional to the concentration of ferrous salt, independent of the concentration of the hydrochloric acid, and is almost doubled when the temperature is increased by 10°.

Approximate proportionality between the rate of reaction and

the concentration of the catalyst is a general feature of catalysis. The explanation of the retarding influence of high concentrations of ferrous chloride is the capability of the salt to form the compound $FeCl_2,NO$ with the catalyst. This is equivalent to a diminution of the effective concentration of the nitric oxide.

In the reversible reaction,

$$FeCl_2,NO \rightleftarrows FeCl_2 + NO,$$

if the initial concentrations of ferrous chloride and nitric oxide are a and b respectively, and the concentration of $FeCl_2,NO$ at equilibrium is x, then the concentrations of free nitric oxide and ferrous chloride are $b - x$ and $a - x$ respectively, and the condition of equilibrium is

$$\frac{(a - x)(b - x)}{x} = K \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

As the ferrous chloride is present in such great preponderance, only a very small fraction of the nitric oxide will exist as such, most of it being present as a complex with the chloride. Any alteration of concentration of ferrous chloride will therefore scarcely affect the concentration of $FeCl_2,NO$, whilst it will have a relatively considerable influence on the smaller quantity, namely, the amount of free nitric oxide. More precisely, in the above equation, when a is very large x is almost equal to b, so that the expression reduces to

$$(a - x)(b - x) = Kb$$

$$\text{or } b - x = \frac{Kb}{a - x} \quad . \quad . \quad . \quad . \quad . \quad \text{(iii)}$$

that is, the concentration of free nitric oxide (the catalyst) is inversely proportional to the concentration of ferrous chloride. As the rate of absorption of oxygen is proportional to the concentration of the catalyst, it is now clear why it should be inversely proportional to the concentration of the ferrous salt. Amongst the various alternative theories put forward to explain catalytic phenomena, the "intermediate compound theory" has been much favoured by various investigators. Whilst in a considerable number of catalytic reactions definite evidence has been brought forward to prove the existence of intermediately formed compounds of the catalyst and one of the reactants, in other cases, problematic loose compounds and "complexes" have been postulated in order to bring the reactions within the purlieus of the theory. Even in cases in which intermediate compounds or complexes have been demonstrated beyond doubt, it does not by any means follow without further argument that such compound formation is the mechanism by which the reaction proceeds. Thus according to

Rideal and Taylor ("Catalysis in Theory and Practice," p. 39), in the preparation of sulphuric acid by the oxidation of sulphur dioxide in the presence of oxides of nitrogen, nitrosylsulphuric acid has been isolated as an intermediate compound, yet evidence is not lacking to show that oxidation can proceed without its formation.

The reaction under consideration in this communication is interesting from the fact that the catalyst (nitric oxide) is able to form compounds with both reactants (ferrous chloride and oxygen). That the capability of the catalyst to form a complex with one of the reacting substances is not always an advantage is illustrated in the effect such a complex formation—$FeCl_2,NO$—has on the rate of oxidation of ferrous chloride. It has been clearly demonstrated in the foregoing experiments that in this case complex formation leads to a retardation of the main reaction.

That the reaction occurs through the alternate formation and reduction of nitrogen peroxide is, however, beyond doubt. The series of reactions is:

$$NO + O = NO_2$$
$$2FeCl_2 + NO_2 + H_2O = 2Fe(OH)Cl_2 + NO$$
$$Fe(OH)Cl_2 + HCl = FeCl_3 + H_2O.$$

The measurable reaction is the first, namely, the oxidation of nitric oxide, the other reactions being immeasurably fast. This explanation is in accordance with the experimental data, namely, *that the rate of reaction is proportional to the concentration of* nitric oxide, and that it is inversely proportional to the concentration of ferrous chloride, as already explained. It is also in accord *with the fact that the velocity is independent of the concentration* of the hydrochloric acid.

It is worthy of note that the oxidation of nitric oxide follows a somewhat different course in the presence and in the absence of water (Abegg, "Handbuch der anorganische Chemie," III, 3, p. 143). With dry oxygen, the reaction is termolecular, according *to the equation*

$$2NO + O_2 = N_2O_4(\rightleftarrows 2NO_2).$$

This reaction has been the subject of very careful investigation in connexion with the lead-chamber process for making sulphuric acid. Lunge and Berl (*Zeitsch. angew. Chem.*, 1906, **19**, 807) and Bodenstein (*Zeitsch. Elektrochem.*, 1910, **16**, 876) have shown conclusively that the reaction leads directly to nitrogen peroxide without intermediate formation of nitrogen trioxide, the formation of which is maintained by Raschig (*Zeitsch. angew. Chem.*, 1904, **17**, 1777). Bodenstein (*loc. cit.*) has made the further interesting

observation that the reaction has a negative temperature coefficient at the ordinary temperature, and proceeds faster at 0° than at 15°.

The experiments described in the foregoing pages show that under our experimental conditions the reaction is unimolecular with reference to the nitric oxide, and it proceeds therefore according to the equation :

$$NO + O = NO_2,$$

the rate of absorption of oxygen being proportional to the concentration of nitric oxide. In this respect it resembles reactions such as the oxidation of sulphur dioxide (Bodländer, *Zeitsch. Elektrochem.*, 1903, **9**, 559, 787) and the oxidation of carbon monoxide (Bodenstein, *Zeitsch. physikal. Chem.*, 1898, **25**, 419), which behave like unimolecular reactions and are classed as surface-reactions.

The equilibrium between nitric oxide and ferrous salts has been the subject of detailed study by Manchot and Zechentmayer (*Annalen*, 1906, **350**, 368). These authors investigated the influence of temperature, pressure, etc., on the amount of nitric oxide in combination with ferrous chloride and ferrous sulphate. At ordinary pressure the formation of the complex is complete at 0°, whilst at 45° the dissociation is more than 80 per cent. With an excess of ferrous salt, the dissociation is, of course, diminished, and we calculate from the results of their experiments on the variation of the equilibrium constant with temperature that, under the conditions of our experiments, the amount of free nitric oxide at 30° is 2·3 times greater than the amount at 20°, being in both instances very small compared with the amount in combination. On this account alone, the velocity of the reaction should be 2·3 times as great at 30° as at 20°. The actual ratio of $k_{30°}$ to $k_{20°}$ was only 1·8, so that increasing the temperature from 20° to 30° leads to a diminution in the velocity of the reaction

$$NO + O = NO_2,$$

a result in agreement with Bodenstein's observations (*loc. cit.*) on the temperature coefficient of the reaction

$$2NO + O_2 = 2NO_2.$$

The mechanism of the catalytic action of nitric oxide on the oxidation of ferrous salts by air or oxygen is thus clearly the oscillation of the oxide of nitrogen between two states of oxidation.

Whilst the "intermediate compound theory" can be employed to advantage in explaining catalysis in homogeneous systems, for purely heterogeneous catalysis in which the catalyst is a solid the adsorption theory is more generally applicable. The mechanism of reactions in the presence of a catalyst (solid), in which there i

no definite evidence of the formation of a compound or complex between the catalyst and either of the reactants, can be sufficiently well explained on the basis of this theory. In most cases of heterogeneous catalysis, adsorption of one or both of the reacting substances by the catalyst in measurable quantities can be shown to take place. The adsorption theory is more acceptable, therefore, than the postulation of unknown compounds or complexes, the existence of which is very problematic.

Here again the existence of adsorption is not, of itself, a proof that the reaction is brought about through its agency. Silica gel (McGavack and Patrick, *J. Amer. Chem. Soc.*, 1920, **42**, 946) has a very marked adsorptive capacity, yet it does not function to any extent as a catalyst in bringing about gaseous reactions. It has been shown by one of us (*J. Soc. Chem. Ind.*, *loc. cit.*) that the experimental data on the rate of addition of hydrogen to olein in the presence of nickel can be explained by the adsorption of hydrogen by the metal together with the dissociation of the adsorbed hydrogen into its atoms. Lewis (T., 1920, **117**, 638) has further shown that the observed velocity constant of such a reaction can be calculated, as regards the order of magnitude, from an expression deduced on the basis of the numher of "favourable" collisions between nickel particles (charged with hydrogen) and olein molecules, "favourable" collisions being defined as occurring between molecules which have received the critical increment of energy.

With a view to the further elucidation of the mechanism of catalytic processes, in particular those involving the addition of hydrogen to unsaturated substances, Taylor (*J. Ind. Eng. Chem.*, 1921, **13**, 75) has measured the adsorption of different gases by finely divided nickel and copper. He finds a greater adsorption by the metals of the unsaturated compound (ethylene) than of hydrogen, and is inclined, on that account, to the view that hydrogenation occurs through the adsorptive power of the metal for the unsaturated body rather than through its power of adsorbing hydrogen. He has not, however, shown that the kinetics of the reaction are in accord with such an explanation.

There are certain points of resemblance between the oxidation of ferrous salts by oxygen in the presence of nitric oxide and the hydrogenation of an unsaturated organic compound like ethylene in the presence of nickel. In the former case, the catalyst (nitric oxide) can form a compound with either ferrous salt or oxygen, whilst in the latter the catalyst (nickel) can adsorb either ethylene or hydrogen.

It has been shown in this communication that the formation of the complex $FeCl_2,NO$ retards the oxidation of ferrous chloride,

whilst the reaction is brought about through the union of the catalyst with the other reactant, oxygen. The point we wish to emphasise is, therefore, the fact that, in catalytic reactions, the existence of a compound or complex between the catalyst and one of the reacting substances is not evidence in itself that such compound formation is the mechanism by which the reaction proceeds. Similarly, in reactions explicable on the adsorption theory of catalysis, the fact that one reactant is adsorbed by the catalyst to a greater extent than the other is not proof that the adsorption of the former is the determining factor. Adsorption *per se* does not determine chemical reactivity, as witness the case of silica gel already mentioned. The final criterion in all cases is the correlation of these facts with reaction velocity.

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LXXXII.—*Ethylstannic Acid and Derivatives.*

By JOHN GERALD FREDERICK DRUCE.

THE potassium salt of ethylstannic acid has been produced by the interaction of stannous chloride, ethyl bromide, and potassium hydroxide:

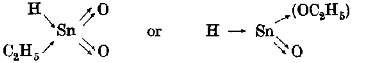
$$SnCl_2 + C_2H_5Br + 4KOH = C_2H_5 \cdot SnO \cdot OK + 2KCl + KBr + 2H_2O.$$

Goldschmidt and Eckardt (*Zeitsch. physikal. Chem.*, 1906, **56**, 385) showed that when "stannous hydroxide" was dissolved in potassium hydroxide solution, potassium hydrogen stannite, $KHSnO_2$, was formed and not the normal salt, K_2SnO_2. They concluded that the hydroxide functioned as a monobasic acid and adhered to the formula H·SnO·OK for potassium hydrogen stannite, advanced by Hantzsch (*Zeitsch. anorg. Chem.*, 1902, **30**, 289), according to which the tin is quadrivalent. To the new acid and methylstannic acid (Meyer, *Ber.*, 1883, **16**, 1442) would similarly be assigned a formula, R·SnO·OH, on account of their apparent analogy with the fatty acids.

Since there can be no oxidation of stannous tin to stannic, it was thought desirable to seek an explanation of these reactions which would take this into account. According to Brauner ("Analysa Kvalitativní," p. 164), the central atom of additive compounds has the property of increasing its positive valency

and its negative valency simultaneously, each by the same number of units, which corresponds in the electronic conception of valency *with the gaining and simultaneous yielding* of valency electrons, so that the total valency remains the same.

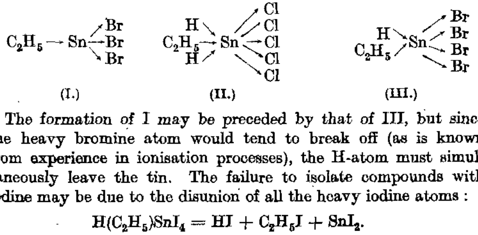
If the direction in which the electrons are attracted be indicated by arrows, the formula for ethylstannic acid becomes



Of these atoms, hydrogen loses *its* valency electron most readily, thus H → is ionogenic. Tin, however, remains positively bivalent (its valency being + 3 − 1).

When treated with concentrated hydrobromic acid, ethylstannic acid dissolved and yielded ethylstannic tribromide, $C_2H_5{\cdot}SnBr_3$. The corresponding iodide could not be produced, and the chloride was isolated in combination with hydrochloric acid.

Denoting by arrows the directions in which the valency electrons are attracted, these compounds can be represented by formulæ I and II:



(I.) (II.) (III.)

The *formation of* I *may be preceded by that of* III, but *since* the heavy bromine atom would tend to break off (as is known from experience in ionisation processes), the H-atom must simultaneously leave the tin. The failure to isolate compounds with iodine may be due to the disunion of all the heavy iodine atoms:

$$H(C_2H_5)SnI_4 = HI + C_2H_5I + SnI_2.$$

Ethylstannic acid dissolved in alkali hydroxide solutions to form salts, but when boiled with excess of the alkali yielded diethylstannic oxide:

$$2C_2H_5{\cdot}SnO{\cdot}OK = (C_2H_5)_2SnO + K_2SnO_3.$$

Other metallic salts and basic salts were obtained by precipitation from the alkali ethylstannates.

The ammonium salt could not be produced, probably on account of the extensive hydrolysis which such a salt would be expected to exhibit (compare, for example, ammonium aluminate, Heyrovský, T., 1920, **117**, 1016).

When heated alone, ethylstannic acid gave a small amount

of ethane, and a large quantity of ethyl alcohol, the residue consisting mainly of stannous oxide.

EXPERIMENTAL.

Ethylstannic Acid, $C_2H_5\cdot SnO\cdot OH$.—A solution of crystallised stannous chloride (30 grams) in warm alcohol (100 c.c.) was added slowly to a cold solution of potassium hydroxide (46 grams) in water (200 c.c.) until the precipitate formed did not redissolve on shaking. The mixture was filtered after one hour, ethyl bromide (20 grams) added to the filtrate, and the mixture shaken at intervals during one hour. After three days the alcohol was evaporated on the water-bath, the solution was faintly acidified with dilute hydrochloric acid, and the white precipitate collected, washed, and dried in the air or over sulphuric acid (Found: Sn = 65·70; C = 13·08; H = 3·51. $C_2H_6O_2Sn$ requires Sn = 65·70; C = 13·28; H = 3·33 per cent.).

When first precipitated, ethylstannic acid is a white, amorphous, gelatinous substance, but on drying it becomes yellowish-brown, transparent, and horny. It is infusible, but decomposes below red heat on heating in the air, a residue of stannic oxide being formed.

When heated strongly in the absence of air, the acid yielded ethane and ethyl alcohol in amounts about 18 per cent. and 55 per cent. respectively of those required by the equations

$$C_2H_5\cdot SnO\cdot OH < \begin{matrix} C_2H_6 + SnO_2 \\ C_2H_6O + SnO \end{matrix},$$

together with a little water (detected by anhydrous copper sulphate) and probably ethylene, as the gas evolved slightly decolorised permanganate solution. The grey residue contained stannous oxide, as it dissolved to a considerable extent in hydrochloric acid, the solution reducing mercuric chloride.

Ethylstannic acid is insoluble in water, alcohol, ether, xylene aniline, chloroform, and acetic acid, but dissolves in dilute minera acids. The freshly prepared acid also dissolves in sodium an potassium hydroxide solutions, but after keeping it becomes almos insoluble in these reagents.

Air-dried material was found to be identical with that kept i a desiccator: a sample, 8·2030 grams, taken from a desiccato weighed 8·2037 grams after remaining in a moist atmosphere fo two days.

Potassium Salt, $C_2H_5\cdot SnO\cdot OK$.—A frequently shaken mixture c potassium hydroxide (1 gram), water (25 c.c.), and ethylstanni acid (4 grams) was filtered after some hours from excess of aci

and the filtrate evaporated in a desiccator until crystals separated (warming was inadvisable). The colourless, deliquescent tablets obtained dissolved easily in water, forming an alkaline solution which became cloudy owing to hydrolysis. Addition of hydrochloric acid precipitated the acid, which redissolved in excess of the precipitant (Found: Sn = 53·4; K = 18·2. $C_2H_5O_2KSn$ requires Sn = 54·4; K = 17·8 per cent.).

Sodium Salt.—This salt was prepared in the same way as the potassium salt, which it resembled in properties (Found: Sn = 57·9; Na = 12·8. $C_2H_5O_2NaSn$ requires Sn = 58·6; Na = 11·3 per cent.).

Copper Salt.—The greenish-blue precipitate obtained by mixing solutions of cupric chloride (1 gram) and potassium ethylstannate (3 grams) was filtered, washed, and dried (Found: Cu = 14·6; Sn = 54·2. $C_4H_{10}O_4CuSn_2$ requires Cu = 14·9; Sn = 56·2 per cent.). The salt did not melt, but blackened on heating. It dissolved in acids with decomposition.

Magnesium Salt.—This was obtained as a white, gelatinous precipitate when solutions of magnesium sulphate (2·5 grams) and potassium ethylstannate (4·4 grams) were mixed together. The horny mass obtained on drying easily disintegrated into an amorphous powder, which decomposed when strongly heated. It was insoluble in water, alcohol, and organic solvents, but dissolved in mineral acids (Found: Sn = 59·12; Mg = 6·46. $C_4H_{10}O_4MgSn_2$ requires Sn = 61·9; Mg = 6·25 per cent.).

Barium Salt.—Attempts to prepare this salt by dissolving ethylstannic acid in barium hydroxide solution failed. It was obtained as a white precipitate, resembling the magnesium salt, by mixing solutions of barium chloride and potassium ethylstannate (Found: Sn = 47·1; Ba = 25·3. $C_4H_{10}O_4BaSn_2$ requires Sn = 47·9; Ba = 27·5 per cent.).

Ethylstannic Tribromide, $C_2H_5·SnBr_3$.

When ethylstannic acid dissolved in hydrobromic acid, b. p. 120°, the concentrated solution deposited colourless, feathery crystals, which did not melt at 310°, but slowly became yellowish-brown. *Ethylstannic tribromide* is soluble in water, but the solution becomes cloudy as ethylstannic acid is regenerated; it also dissolves in alcohol (Found: Sn = 29·87; Br = 61·40. $C_2H_5Br_3Sn$ requires Sn = 30·67; Br = 61·85 per cent.).

Ethylchlorostannic Acid, $H_2SnEtCl_5$.

This acid was obtained by dissolving ethylstannic acid in concentrated hydrochloric acid and leaving the solution in a desiccator

over solid sodium hydroxide. The colourless, deliquescent prisms obtained were decomposed by water, and also on heating (Found: Sn = 35·24; Cl = 55·0. $C_2H_7Cl_5Sn$ requires Sn = 35·15; Cl = 55·7 per cent.).

Potassium Salt, $K_2SnEtCl_5$.—Potassium chloride (1·5 grams) and ethylchlorostannic acid (3·3 grams) were dissolved in dilute hydrochloric acid, and colourless, deliquescent, infusible crystals separated after the concentrated solution had stood over solid sodium hydroxide in a desiccator. The salt dissolved in water to a clear solution, which became cloudy on boiling. Hydrogen sulphide gave a yellow precipitate when passed into a hydrochloric acid solution of the salt (Found: Sn = 30·2; Cl = 44·1. $C_2H_5Cl_5K_2Sn$ requires Sn = 29·5; Cl = 43·9 per cent.).

Aniline Salt, $(C_6H_5{\cdot}NH_2)_2,H_2SnEtCl_5$.—By concentrating a solution of aniline hydrochloride (2·6 grams) and ethylchlorostannic acid (3·3 grams) in 30 c.c. of dilute hydrochloric acid, small rosettes of granular crystals were obtained. The salt did not melt at 305°. It dissolved in water to a clear, strongly acid solution, and was soluble in methyl and ethyl alcohols, but not in other organic solvents. The aqueous solution gave a flocculent precipitate of ethylstannic acid on boiling (Found: Sn = 22·6; Cl = 35·0. $C_{14}H_{21}N_2Cl_5Sn$ requires Sn = 23·1; Cl = 34·6 per cent.).

Diethylstannic Oxide.

Five grams of ethylstannic acid were gradually added to 100 c.c. of a boiling, 10 per cent. solution of sodium hydroxide. Heating was continued for an hour and the insoluble residue was filtered, washed until free from alkali, and dried. The white diethylstannic oxide was infusible, and insoluble in water, but dissolved in hot hydrochloric acid solution (compare Pfeiffer, *Ber.*, 1911, **44**, 1269) (Found: Sn = 61·4. Calc., Sn = 61·6 per cent.).

Basic Salts of Ethylstannic Acid.

The following basic salts of ethylstannic acid were obtained a[s] amorphous precipitates on adding solutions of the metal chloride[,] sulphate, or nitrate to a solution of potassium ethylstannate[.]

Silver salt, brown, approximating in composition to the formul[a] $Ag_2O,C_2H_5{\cdot}SnO{\cdot}OAg$.

Zinc salt, white, containing about 19 per cent. of tin and 57 pe[r] cent. of zinc.

Mercuric salt, brownish-black.

Cobalt salt, blue, becoming pale pink on drying and approximati[ng] in composition to the formula $CoO,(C_2H_5{\cdot}SnO{\cdot}O)_2Co$.

Nickel salt, pale green; approximate composition,

$$NiO,(C_2H_5\cdot SnO\cdot O)_2Ni.$$

Manganese salt, white, turning brown.

Strontium salt, white, containing about 18 per cent. of tin and 24·5 per cent. of strontium.

All these basic salts were decomposed by acids.

In conclusion, the author thanks Dr. J. Heyrovský, of Prague University, for directing his attention to Prof. Brauner's views on complex salts.

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LXXXIII.—*Note on Dithiocarbazinic Acid.*

By SIMA M. LOSANITCH.

ZEISE (*Jahresber.*, 1858, **4**, 96) has shown that ammonium dithiocarbamate is formed by the interaction of ammonia and carbon disulphide,

$$CS_2 + 2NH_3 = NH_2\cdot CS\cdot SNH_4.$$

In a former publication (*Ber.*, 1891, **24**, 3021) I have shown that when reaction takes place between either ammonia or an aliphatic amine and carbon disulphide in the presence of an aromatic amine, salts of aryldithiocarbamic acids are formed. Moreover, it has been established that the less basic amine is always directly connected with the carbon of the dithiocarbamic acid, and the more basic *amine appears regularly as the cation of the salt :*

$$CS_2 + R\cdot NH_2 + C_6H_5\cdot NH_2 = C_6H_5\cdot NH\cdot CS\cdot SNH_3R.$$

It will be shown in the present paper that the reaction between carbon disulphide and hydrazine hydrate, which leads to the formation of hydrazine dithiocarbazinate (Curtius and Keidenreich, *Ber.*, 1894, **27**, 58; *J. pr. Chem.*, 1895, [ii], **52**, 485), may be extended in a similar way when it takes place in the presence of ammonia or an aliphatic amine. The reaction occurs at room temperature as follows :

$$CS_2 + N_2H_4,H_2O + R\cdot NH_2 = NH_2\cdot NH\cdot CS\cdot SNH_3R + H_2O,$$

where R = H or Me.

In this case ammonia or the aliphatic amine, being the stronger

base, forms the cation of the salt, and hydrazine, the weaker base, is linked directly to the carbon atom as the hydrazide group. In support of the constitution of these salts is the fact that from both of them only one ester, $NH_2\cdot NH\cdot CS\cdot SMe$, is obtained by the action of methyl iodide, and thereby is excluded the other possible constitution for these compounds, namely, $NHR\cdot CS\cdot SN_2H_5$.

It has been further found that by the action of an excess of methyl iodide one atom of nitrogen is eliminated in both cases, and the compound $SMe\cdot CS\cdot NMe\cdot NMe\cdot CS\cdot SMe$ is formed.

Analogous to the above reactions is the formation of hydrazine phenyldithiocarbazinate by the simultaneous action of hydrazine hydrate and phenylhydrazine upon carbon disulphide,

$$CS_2 + N_2H_4,H_2O + C_6H_5\cdot NH\cdot NH_2 = CS<^{NH\cdot NH\cdot C_6H_5}_{S\cdot N_2H_5} + H_2O.$$

Owing to the presence of the hydrazide group the dithiocarbazinates readily undergo change. When heated with acids, they decompose into their components:

$$NH_2\cdot NH\cdot CS\cdot SNH_4 + 2HCl = NH_4Cl + N_2H_4,HCl + CS_2.$$

In aqueous solution they furnish slowly on heating hydrogen sulphide, ammonium sulphide, ammonia (or an amine), sulphur, and a crystalline product of acid reaction, the nature of which has not yet been established.

Experimental.

Ammonium Dithiocarbazinate, $NH_2\cdot NH\cdot CS\cdot SNH_4$.

This salt is obtained when to an alcoholic solution of hydrazine hydrate containing a large excess of ammonia (to prevent the formation of the hydrazine salt) is slowly added with cooling the corresponding quantity of carbon disulphide. *Ammonium dithiocarbazinate* first separates as a yellow, oily mass, which soon crystallises. It dissolves easily in water, and slightly in alcohol, is insoluble in ether, and crystallises from diluted alcohol in yellow, transparent prisms, which melt and decompose at 114° (Found: C = 9·9; H = 5·8; N = 33·5; S = 51·7. $CH_7N_3S_2$ requires C = 9·6; H = 5·6; N = 33·6; S = 51·2 per cent.).

The *methyl* ester, $NH_2\cdot NH\cdot CS\cdot SMe$, is obtained when a solution of the ammonium salt or other salt of dithiocarbazinic acid in diluted alcohol is treated with methyl iodide (1 mol.). It is easily soluble in alcohol, and is insoluble in water, and crystallises from alcohol or benzene in colourless needles or prisms melting at 82° (Found: C = 19·00; H = 4·99; N = 22·60; S = 52·05. $C_2H_6N_2S_2$ requires C = 19·67; H = 4·91; N = 22·95; S = 52·46 per cent.).

Methyl bis-Methyldithiocarbamate, SMe·CS·NMe·NMe·CS·SMe.

This compound is formed either directly from the ammonium salt or other salt of dithiocarbazinic acid and two molecules of methyl iodide, or from the preceding ester and one molecule of the same reagent. It crystallises from alcohol or benzene in white needles, which melt between 118° and 119° (Found: N = 11·70; S = 53·30. $C_6H_{12}N_2S_4$ requires N = 11·67; S = 53·33 per cent.).

Methylammonium Dithiocarbazinate, NH_2·NH·CS·SNH_3Me.

This salt has been obtained from its components with cooling. It is easily soluble in water, but dissolves to a much smaller extent in alcohol, from which it crystallises in yellow needles melting and decomposing at 112° (Found: N = 30·32. $C_2H_9N_3S_2$ requires N = 30·22 per cent.).

Ethylammonium dithiocarbazinate and *tetramethylammonium dithiocarbazinate* have been prepared in a similar manner from ethylamine and tetramethylammonium hydroxide respectively.

Hydrazine Phenyldithiocarbazinate, NHPh·NH·CS·SN_2H_5.

The salt has been obtained from its components in alcoholic solution as a white product, which crystallises from alcohol, and melts and decomposes at 110° (Found: S = 30·01. $C_7H_{12}N_4S_2$ requires S = 29·63 per cent.).

Hydrazine Phenyldithiocarbamate, NHPh·CS·SN_2H_5.

When carbon disulphide reacts with aniline and hydrazine hydrate in alcoholic solution, hydrazine dithiocarbazinate crystallises out and *hydrazine phenyldithiocarbamate* remains in solution, ultimately decomposing in the manner described above.

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[*Received, March 8th*, 1921.]

LXXXIV.—*Reduction of Emulsified Nitro-compounds. Part I. β-Phenylhydroxylamine from Nitrobenzene.*

By ARTHUR LAPWORTH and LEONORE KLETZ PEARSON.

A SURVEY of the methods available for the manufacture of phenacetin, of which drug there was a dearth in this country during the early stages of the war, led to inquiries being made as to avail-

able supplies of *p*-aminophenol, and during the course of these inquiries it was suggested by Dr. Herbert Levinstein that a simplified method for manufacturing β-phenylhydroxylamine from nitrobenzene, involving, for example, the use of cheap sulphides as reducing agents and aqueous solutions, was much to be desired.

It was well known that the desired reduction can be effected by the use of ammonium hydrosulphide, but in practice alcoholic solutions were used. Thus Willstätter and Kubli obtained β-phenylhydroxylamine from nitrobenzene in very fair yield in this manner (*Ber.*, 1908, **41**, 1936). It occurred to one of us that an aqueous solution might possibly be used if an emulsifying agent were added in order to facilitate the intimate admixture of the two non-miscible fluids.

Mixtures of nitrobenzene and ordinary ammonium sulphide solution with enough kieselguhr to form a permanent emulsion after agitation were therefore made, and in one instance the whole of the nitrobenzene disappeared during the night. On filtering, washing the residue with water, and saturating the united filtrates with common salt, crystalline β-phenylhydroxylamine was obtained in quantity approximating, after removal of sulphur, to 50 per cent. of that theoretically possible.

The effect of replacing ammonium sulphide with the cheaper sodium salt was then examined under a variety of conditions and by using solutions made from commercial sulphide with enough hydrochloric acid or hydrogen sulphide to convert the salt into hydrosulphide, satisfactory results were obtained, whilst trouble due to free sulphur was eliminated. During the course of these experiments it occurred to one of us (L. K. P.) to examine the effect of adding calcium chloride to the system at the beginning of the reaction, and a decided rise in the yield of product was observed. As it seemed probable that the principal effect of the added calcium chloride was an improved emulsification, the kieselguhr was ultimately omitted, and without ill effect on the yield of product. In these circumstances, the addition of calcium chloride causes the separation of a finely divided precipitate, doubtless calcium hydroxide or "basic" sulphides, and in presence of this emulsification takes place readily; there is, however, little doubt that the condition of the system as to its state of alkalinity is simultaneously and favourably affected, and it is not altogether a matter of indifference how much calcium chloride is added.

By regulating the conditions as to concentration, the bulk of the phenylhydroxylamine obtained in the modified process may be made to separate in solid form, but, if filtered off in presence of the precipitate of alkaline calcium compounds, it tends to oxidise i

the air with considerable rise of temperature. In order to dissolve these compounds and to reduce alkalinity, we have found it most convenient to add ammonium chloride, which effects both purposes and does not tend to cause separation of sulphur. Possibly, on a large scale, a saving in expense would be effected by the cautious addition of hydrochloric acid, for example, and the use of an ammonium salt in minimal quantity, but we have not studied this matter in detail.

Preparation of β-Phenylhydroxylamine from Nitrobenzene.

The following procedure gives, with a little practice, yields of β-phenylhydroxylamine amounting to about 72—74 per cent. of that theoretically possible and without extraction of the aqueous mother-liquors. For much larger quantities of material it would perhaps be desirable to modify the procedure; for example, to operate in the first instance with a smaller proportion of water in the system and to regulate the temperatures at different stages by suitable additions of ice.

A solution of sodium sulphide is made by dissolving 27·6 grams of the moist crystals ($Na_2S,9H_2O$) in 21·8 c.c. of water, placing this in a narrow cylinder and cautiously adding, with constant stirring and by means of a funnel the lower end of which passes to the bottom of the cylinder, 10·5 c.c. of hydrochloric acid (D 1·16). The resulting solution of sodium hydrosulphide and chloride is placed at about 15° in a stoppered vessel * with 5 grams of nitrobenzene and 5 grams of calcium chloride dissolved in the minimal quantity of water. The whole, when vigorously agitated, emulsifies and subsequently needs shaking occasionally. The temperature rises, but should not exceed 30°, and the colour of the liquid becomes orange to deep orange-red. After an interval, usually about three-quarters of an hour, the oil becomes thicker and crystals appear. At the critical stage, the whole of the oil has disappeared and this point should be noted carefully, either by the use of a lens or by adding ammonium chloride to a test portion. At this stage, usually about one and a half hours from the beginning, 6 grams of ammonium chloride are added and the whole is shaken, when the inorganic deposits pass almost completely into solution. On filtering, about 3·3 grams of nearly pure, crystalline β-phenylhydroxylamine are retained on the filter.

Many variations on the foregoing procedure have been tried, but without any improvement; such have been, for example,

* As the reaction mixture absorbs oxygen somewhat rapidly, precautions to prevent this effect or to minimise its results may be necessary.

(1) the preparation of the hydrosulphide solution with gaseous hydrogen sulphide instead of by addition of hydrochloric acid; (2) the use of sodium sulphide instead of hydrosulphide, in which case the reduction process is slower and the end result less certain; (3) variation in the proportion of calcium chloride used.

The authors desire to express their indebtedness to the Department of Scientific and Industrial Research for a grant to one of us (L. K. P.), and also for permission to publish these results.

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LXXXV.—*Reduction of Emulsified Nitro-compounds. Part II. Some Extensions of the Method.*

By ROBERT DOWNS HAWORTH and ARTHUR LAPWORTH.

AN emulsification process such as that described in Part I (this vol., p. 765) is applicable without considerable modification only to such nitro-compounds as are fluid at the ordinary or slightly elevated temperatures. Such nitro-compounds are exceptional in the aromatic series, and only nitrobenzene and *o*-nitrotoluene have been examined. The authors were persuaded by Dr. Herbert Levinstein to ascertain whether the method might not be extended to solid nitro-compounds by introducing into the system a fluid, such as benzene, insoluble in water but capable of wholly or partly dissolving the nitro-compound present. It was found that satisfactory results could be obtained in many instances, as many nitro-compounds are sufficiently soluble in benzene for the purpose, and, further, that, providing the nitro-compound is finely divided, it is not always necessary that it should initially be entirely dissolved in the quantity of benzene used, since, as reduction proceeds, undissolved nitro-compound passes quickly enough into solution. This modification of the original method is especially attractive in such cases where substituted hydroxylamines are the main products, for these substances are usually sparingly soluble in benzene and may often be separated with but slight loss owing to solubility, by mere filtration after addition of ammonium chloride at the critical stage in the reduction.

The reduction by sulphides and hydrosulphides of some of the

nitro-compounds investigated has already been studied by previous workers. This is true, for example, of phenyl-, *p*-tolyl-, and α-naphthylhydroxylamines, all of which were made by Willstätter (*Ber.*, 1908, **41**, 1936) by use of ammonium sulphide in alcoholic solution. The mode of applying sulphides as reducing agents described in the present communications does not appear to have been used before.

EXPERIMENTAL.

Except where, in the text, a statement to the contrary is made, the procedure adopted in each case was as follows :—

The nitro-compound, finely divided if necessary, was dissolved or suspended in from one and a quarter to twice its bulk of benzene, and placed in a stoppered bottle with the requisite quantity of the cold solution of sodium hydrosulphide. The calcium chloride, dissolved in the minimum necessary amount of water, was then added, and the whole shaken to form an emulsion, the shaking being occasionally repeated, if, for example, external cooling was necessary or the emulsion showed signs of deterioration. A lens was used to observe the appearance or disappearance of crystals in the mass.

The hydrosulphide solution was always prepared as described in Part I (*loc. cit.*) and with the same proportion of reagents; namely, hydrated sodium sulphide ($Na_2S,9H_2O$), 275 grams; water, 200 c.c., and hydrochloric acid (D=1·16), 97 c.c. This solution contains 10·9 per cent. of NaSH, and in the description of each experiment is given the weight of this solution taken.

Analysis of Substituted Hydroxylamines.

In a few cases where new substances have been isolated elementary analyses were carried out. In almost every other case the composition of the hydroxylamine was simply checked by an estimation of the quantity of stannous chloride oxidised in accordance with the equation

$$R \cdot NH \cdot OH + SnCl_2 + 2HCl = R \cdot NH_2 + SnCl_4 + H_2O,$$

the operations being carried out much as in the usual method for estimation of nitro-groups, the excess of stannous chloride being measured after addition of Rochelle salt and bicarbonate by titration with a standard solution of iodine. The process was tested and found accurate with phenylhydroxylamine, and apparently gave satisfactory results in all the other cases tried. For brevity in citing the results of analyses, the quantity of stannous chloride oxidised by the hydroxylamine is expressed in volumes of $N/10$-$SnCl_2$.

p-Chlorophenylhydroxylamine from p-Chloronitrobenzene.

A solution of 11 grams of *p*-chloronitrobenzene (m. p. 83°) in 15 c.c. of benzene was mixed with 115 grams of the hydrosulphide solution and the whole emulsified by shaking with 10 grams of calcium chloride in water. The temperature was kept below 30° with the aid of external cooling. Crystals soon began to separate from the orange fluid. After one and a quarter hours, 10 grams of solid ammonium chloride were added and the whole was well shaken and filtered, when about 6·6 grams of nearly pure *p*-chlorophenylhydroxylamine remained on the filter; this quantity represents about 67—68 per cent. of that theoretically possible and only 0·22 gram of the product was subsequently found in the aqueous mother-liquor, whilst evaporation of the benzene layer yielded little but unchanged nitro-compound.

In a repetition of the process lasting an hour and a half, with the same quantities of materials, the weight of crystalline solid filtered off was 7·1 grams.

For identification, the substance was crystallised from hot benzene and then melted at 86·5° (compare Bamberger, *Ber.*, 1895, **28**, 245) (0·5008 gram required 3·44 c.c. of $N/10$-$SnCl_2$, whence NH·OH=22·2. C_6H_4Cl·NH·OH requires NH·OH=22·3 per cent.).

On oxidation with acid dichromate and subsequent distillation in a current of steam, it gave *p*-chloronitrosobenzene melting at 86° (Bamberger, *loc. cit.*, p. 249).

p-Bromophenylhydroxylamine from p-Bromonitrobenzene.

For this reduction were taken:—*p*-bromonitrobenzene (m. p. 146°), 5 grams; benzene, 7 c.c.; the hydrosulphide solution, 52 grams; calcium chloride, 5 grams, in water. The process took place much as in the preceding case, and after one and a half hours, 5 grams of solid ammonium chloride were added and the solution was filtered. The solid *p*-bromophenylhydroxylamine, thus separated, weighed 3·2 grams, or about 65 per cent. of the maximum possible; about 0·12 gram was found in the aqueous part of the filtrate. After recrystallisation from hot benzene the substance melted at 90° (Bamberger, *loc. cit.*, p. 1221). On oxidation with ice-cold, acid dichromate, 2 grams yielded 1·32 grams of *p*-bromonitrosobenzene melting at 91·5° (*loc. cit.*).

p-Iodophenylhydroxylamine from p-Iodonitrobenzene.

Five grams of *p*-iodonitrobenzene (m. p. 166°) were reduced under conditions similar to those employed in the two preceding cases

and for about the same length of time. Approximately 3·0 grams of *p*-iodophenylhydroxylamine, or 64 per cent. of the amount theoretically possible, was at once obtained in solid form. The product, after crystallisation from hot benzene, melted at 103° and was converted by dichromate mixture into *p*-iodonitrosobenzene melting at 101·5° (compare Bamberger, *loc. cit.*, p. 249).

p-*Tolylhydroxylamine from* p-*Nitrotoluene.*

p-Nitrotoluene was the first solid nitro-compound which the authors studied, and it gave considerable trouble, as reduction by the emulsification process herein described takes place somewhat slowly, and if unduly prolonged leads to loss owing to formation of *p*-toluidine. The best results were obtained with the following conditions:—

p-Nitrotoluene (10 grams) in benzene (20 c.c.) is emulsified by shaking with 147 grams of the hydrosulphide solution and 10 grams of calcium chloride in water. After twenty-four hours at the laboratory temperature the solution is usually yellowish-green, and crystals are present, which may be secured by adding ammonium chloride (15 grams), shaking thoroughly, and filtering. About 4·8 grams of fairly pure *p*-tolylhydroxylamine remain on the filter, and after a recrystallisation from hot benzene the substance melts sharply at 98° (Bamberger, *loc. cit.*, p. 245); about 0·47 gram may be obtained by extraction of the aqueous part of the filtrate (0·9652 gram required 7·88 c.c. of $N/10$-$SnCl_2$, whence NH·OH=25·7. C_7H_7·NH·OH requires NH·OH=26·0 per cent.).

On oxidation, 2 grams gave 1·21 grams of *p*-nitrosotoluene, volatile in steam and melting at 47° (Bamberger, *loc. cit.*, p. 247).

Reduction of o-*Nitrotoluene.*

This compound, which, owing to its low melting point, does not require the addition of benzene, has not given satisfactory results. The maximum production of *o*-tolylhydroxylamine observed has been after seventy-two hours, and was about 15 per cent. of that theoretically possible. As crystals do not separate, this estimate has been based on the analysis of the total, washed, ethereal extract, after addition of ammonium chloride to dissolve calcium compounds; the method of analysis was that used by Goldschmidt in his well-known researches on the reduction of nitro-compounds (*Zeitsch. physikal. Chem.*, 1904, **48**, 424, 435; 1905, **56**, 1385; 1910, **71**, 437). No difficulty was experienced in obtaining more direct qualitative proof of the presence of *o*-tolylhydroxylamine in the ethereal extract specified, for on oxidising with acidified dichromate solution and

distilling with a current of steam o-nitrosotoluene passed over with the first few c.c. of distillate, set to a pale yellow solid, and separated from alcohol in white needles melting at 71° (*Ber.*, 1895, **28**, 245).

As no amines, or only traces, were formed in the foregoing experiments, it may be concluded that the reduction of o-nitrotoluene is exceptionally slow, and it seems not improbable that failure to increase the yield by prolonged action of the agent is due to deterioration of the emulsifying precipitate of calcium compounds. This effect, in conjunction with the pressure of the hydrogen sulphide developed at temperatures much above the ordinary, renders it impracticable to heat in an open vessel when reducing with hydrosulphide and calcium chloride emulsions.

Experiments were tried in which o-nitrotoluene was emulsified with hot sodium hydrosulphide solution, using kieselguhr as emulsifying agent, but only o-toluidine was obtained; with calcium chloride present also, the hydrogen sulphide pressure was inconvenient and very little reduction was effected.

It may be added that Bamberger experienced unusual difficulty in obtaining o-tolylhydroxylamine in solid form, and in its slight tendency to separate from benzene it is evident that this compound and o-chlorophenylhydroxylamine differ markedly from the corresponding p-compounds.

Reduction of o-*Chloronitrobenzene.*

When this compound is reduced in benzene solution emulsified with the sodium hydrosulphide solution and calcium chloride at the ordinary temperature for two hours, no separation of the hydroxylamine occurs; but if ammonium chloride be then added, the aqueous layer extracted with ether, and the residues obtained by evaporation of the benzene and the ethereal extract combined, an oily product is left which, when tested by Goldschmidt's standard iodine method, gives results indicating a total production of o-chlorophenylhydroxylamine amounting to 62 per cent. of that theoretically possible. The substance itself has not been isolated, but the following experiment indicates that the oil in question may be utilised for preparing its derivatives.

The oil (2·0 grams) was oxidised with 4 grams of potassium dichromate in 270 c.c. of water containing 10 c.c. of concentrated sulphuric acid. On finally passing in a current of steam there passed over with the first 20 c.c. of distillate a pale yellow oil which solidified on cooling, yielding 1·30 grams of o-*chloronitrosobenzene* (Found: C=50·8; H=3·1; Cl=24·9. C_6H_4ONCl requires C=50·9; H=2·9; Cl=25·1 per cent.). The new substance dissolves readily in ether, alcohol, chloroform, benzene, and hot light petrol

eum. It separates from alcohol in colourless needles melting at 56—57°.

m-*Bromophenylhydroxylamine from* m-*Bromonitrobenzene.*

The quantities used were :—*m*-bromonitrobenzene (m. p. 56°), 5 grams; benzene, 7 c.c.; sodium hydrosulphide solution, 74 grams; calcium chloride, 4 grams, and water. Three hours after emulsification ammonium chloride (5 grams) was added and the whole filtered. There remained on the filter, 2·53 grams of solid *m*-bromophenylhydroxylamine, or about 55 per cent. of the amount theoretically possible, an additional 0·2 gram remaining in the aqueous layer of the filtrate. The recrystallised product melted at 66° (compare *Ber.*, 1896, **29**, 864) and was converted by acidified dichromate solution into *m*-bromonitrosobenzene melting at 78° (compare *Ber.*, 1898, **31**, 1517, *anm.*). The nitroso-compound was analysed (Found: C=38·7; H=2·2; Br=42·8. Calc., C=38·8; H=2·2; Br=43·0 per cent.).

m-*Chlorophenylhydroxylamine*, $C_6H_4Cl\cdot NH\cdot OH$, *from* m-*Chloronitrobenzene.*

For this reduction 11 grams of *m*-chloronitrobenzene (m. p. 44·5°) were taken, with benzene (15 c.c.), sodium hydrosulphide solution (147 grams), calcium chloride (10 grams), and the necessary water. The colour of the liquid passed through green to pale orange, and after two and a half hours crystals separated. Ammonium chloride (10 grams) was added, the whole shaken and filtered, when 5·8 grams of nearly pure *m*-chlorophenylhydroxylamine were obtained in solid form. The filtrate yielded only 0·2 gram more.

m-*Chlorophenylhydroxylamine* crystallises from benzene in colourless plates melting at 49°, and dissolves more readily in benzene, light petroleum, and water than do its isomerides (Found: C=50·1; H=4·2; Cl=24·6. C_6H_6ONCl requires C=50·2; H=4·1; Cl=24·7 per cent.). An alcoholic solution of the compound after exposure to air deposited pale yellow needles melting at 96°, and these were identified as 3 : 3′-dichloroazoxybenzene, convertible into 3 : 3′-dichloroazobenzene melting at 100·5° by distillation with iron filings.

m-*Chloronitrosobenzene*, $C_6H_4Cl\cdot NO$.

This substance was made by oxidising the preceding one with ice-cold dichromate solution in presence of excess of sulphuric acid and finally expelling the product with a current of steam, when it passed over as a green fluid. It dissolves readily, forming green solutions in benzene, alcohol, ether, chloroform, or acetone,

and crystallises from benzene in colourless needles melting at 72° (Found: C=50·8; H=3·0; Cl=24·9. C_6H_4ONCl requires C=50·9; H=2·9; Cl=25·1 per cent.).

α-Naphthylhydroxylamine and α-Naphthylamine from α-Nitronaphthalene.

A solution of 10 grams of α-nitronaphthalene in benzene (15 c.c.) was emulsified with the hydrosulphide solution (115 grams) and calcium chloride (10 grams) in water; the temperature rose rapidly, but was kept below 30° by external cooling. The colour changed slowly to chocolate, and crystals began to separate after four hours; half an hour later ammonium chloride (11 grams) was added, when, on filtration, about 7·75 grams of grey crystals were obtained, which were fairly pure α-naphthylhydroxylamine. No α-naphthylamine was detected either in the crystals or in the filtrate.

Recrystallisation of the solid from benzene gave pale yellow crystals which fused at 78—78·5°, but after exposure in a desiccator for some days melted at 82—83°. These properties and the following analysis of the more fusible solid are in agreement with the observations of Scheiber, who found that this form is a monohydrate (*Ber.*, 1904, **37**, 3055) (0·8992 required 5·28 c.c. of $N/10$-$SnCl_2$, whence NH·OH=18·5. $C_{10}H_7$·NH·OH,H_2O requires NH·OH=18·1 per cent.).

Even when the proportions of hydrosulphide solution and calcium chloride taken were double those given above and the time of reduction was increased to twelve hours, the main product was still the hydroxylamine, very little naphthylamine being formed. It was not found effective to heat the system, owing, doubtless, to deterioration of the emulsion. As some interest appeared to attach to the possibility of reducing α-nitronaphthalene to α-naphthylamine by an emulsification process, a reversion to the original plan of using kieselguhr as an emulsifying agent was tried. Using α-nitronaphthalene, benzene, and sodium hydrosulphide, but adding kieselguhr instead of calcium chloride and then heating on the water-bath for eight hours, yields of α-naphthylamine up to about 73 per cent. of the theoretical quantity were obtained, but it was soon evident that much time might be spent in attempts to improve the rough process, and the experiments were not further proceeded with.

α-Hydroxylaminoanthraquinone and α-Aminoanthraquinone from α-Nitroanthraquinone.

α-Nitroanthraquinone may be reduced to the hydroxylamine o amino-compound respectively by making suitable variations in th

concentration of hydrosulphide solution. The great difficulty in preparing this nitro-compound in a pure state, however, detracts considerably from the interest of this application of the process.

On emulsifying 5 grams of α-nitroanthraquinone (m. p. 219°) in 150 c.c. of benzene with 56 grams of the hydrosulphide solution and 5 grams of calcium chloride in water, a green coloration, due to formation of soluble salts of the hydroxylamine, is observed (compare *Ber.*, 1882, **15**, 1790; 1883, **16**, 367; 1896, **29**, 2934). The temperature rises, and efficient cooling is necessary to keep the temperature below 30°. After five minutes a brown powder begins to separate, and soon the whole sets to a thick paste which gradually becomes red in colour. If the whole be allowed to remain overnight, subsequent addition of ammonium chloride (5 grams) and filtration yields 4 grams of brick-red, powdery α-aminoanthraquinone, which, however, requires purification from a trace of unchanged nitro-compound, and then melts at 242°.

Using less benzene than in the preceding description and allowing the whole to remain for twenty-four hours, a similar result is obtained, but the quantity of unchanged nitro-compound is larger.

It has not been found possible wholly to arrest the reduction of α-nitroanthraquinone at the intermediate hydroxylamine stage, but by using more dilute hydrosulphide solution than that adopted as suitable in other cases, and by operating for a much shorter time, fair yields of the hydroxylamine in a somewhat impure form may be obtained. The best result was obtained as follows:—

The nitroanthraquinone (5 grams) was suspended in benzene (20 c.c.) and, with the aid of calcium chloride (3 grams), emulsified with 21 grams of the standard hydrosulphide solution which had previously been diluted to 75 c.c. with water; after forty-five minutes ammonium chloride (3 grams) was added and the solid filtered off. By extracting the solid with dilute sodium hydroxide solution and subsequently acidifying, 3·6 grams of α-hydroxylaminoanthraquinone, or 73 per cent. of the theoretical amount, were obtained; after recrystallisation from hot acetone it formed reddish-brown needles melting at 137—139° (0·7412 required 3·16 c.c. of $N/10$-$SnCl_2$, whence NH·OH=13·4. $C_{14}H_9O_3N$ requires NH·OH=13·4 per cent.).

Reduction of m-*Dinitrobenzene and* 2:4-*Dinitrotoluene by the Emulsification Process.*

A considerable amount of work on the reduction of dinitro-compounds has been carried out by previous workers. The nitro-hydroxylamine has been obtained from *m*-dinitrobenzene by Wohl

(D.R.-P. 84138, 1895) and Brand (*Ber.*, 1905, **38**, 4006), using the zinc-dust and electrolytic reduction method respectively. Brand (*J. pr. Chem.*, 1906, [ii], **74**, 449) found that partial reduction of dinitro- and polynitro-derivatives of benzene by sulphides and polysulphides of sodium and ammonium leads mainly to formation of azoxy-compounds or amines, according as there is excess or deficit of hydroxyl ions. Flürscheim and Simon (T., 1908, **93**, 1463), Cohen and Dakin (*ibid.*, 1902, **81**, 26), and Cohen and McCandlish (*ibid.*, 1905, **87**, 1257) may also be consulted.

Application of the emulsification method to *m*-dinitrobenzene, dissolved or suspended in benzene, showed that considerable dilution of the standard hydrosulphide solution is necessary in order to restrain the unusually rapid rise in temperature. The solid product obtained on addition of ammonium chloride was brown to orange, and only 3 : 3′-dinitroazoxybenzene was isolated from it. Reduction of 2 : 4-dinitrotoluene gave similar results, but 3 : 3′-dinitro-4 : 4′-dimethylazoxybenzene was isolated from the product and identified by conversion into 2-nitro-*p*-toluidine by reduction with alcoholic sodium hydrosulphide.

Reduction of Nitroanilines and of p-*Nitrophenol.*

The difficulty in arresting the reduction of nitroaniline at the hydroxylamine stage has already been realised by previous workers (Goldschmidt, *Zeitsch. physikal. Chem.*, 1905, **56**, 1385; Flürscheim and Simon, T., 1908, **93**, 1463; Elbs, *Zeitsch. Elektrochem.*, 1901, **1**, 134).

When the emulsification method is applied to *m*- or *p*-nitroaniline dissolved or suspended in benzene, slow reduction occurs, but no solid is obtained on addition of ammonium chloride, as the products are too freely soluble in benzene; no evidence of the formation of any substituted hydroxylamine was obtained. The authors have not thought it worth while to work out the optimum conditions for preparing the diamines, which are the main products of the reaction, as the method does not promise to be advantageous in such instances.

The only nitrophenol investigated was *p*-nitrophenol. The emulsification process is difficult to apply in these cases owing to the sparing solubility of the sodium derivatives of the nitrophenol and to the exceptionally slow progress of the reaction. The results obtained on attempting to isolate any reduction products were entirely negative, and no attempt was made to extend the observations in this unpromising field.

Summary.

The emulsification process described in Part I has been extended to the reduction of *o*-nitrotoluene and to a number of nitro-compounds of the aromatic series which are solid at the ordinary temperature.

o-Nitrotoluene and *o*-chloronitrobenzene, the former as such and the latter when dissolved in benzene, do not at once yield solid hydroxylamines, but give oils containing about 15 and 62 per cent. respectively of the corresponding hydroxylamines.

The process gives satisfactory results with *p*-nitrotoluene, *p*-chloronitrobenzene, *p*-iodonitrobenzene, *m*-chloronitrobenzene, *m*-bromonitrobenzene, α-nitronaphthalene, using solutions or suspensions of these compounds in benzene, the β-substituted hydroxylamines being secured at once in solid form and in yields usually exceeding, sometimes considerably, 50 per cent. of the amount theoretically possible, a few units per cent. only remaining in the filtrate.

α-Nitroanthraquinone dissolved or suspended in benzene yields either the corresponding solid hydroxylamine or solid amino-compound, according to the conditions. *m*-Dinitrobenzene and 2 : 4-dinitrotoluene give mainly the solid dinitroazoxy-compounds.

m-Nitroaniline and *p*-nitroaniline are reduced to the corresponding diamines, but these remain dissolved. The process is not applicable to *p*-nitrophenol.

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LXXXVI.—*Determination of the Composition of Mixtures of Eugenol and* iso*Eugenol Benzoates by means of Melting Points.*

By Phyllis Violet McKie.

In the preparation of vanillin from eugenol (oil of cloves), through *iso*eugenol, a mixture of eugenol and *iso*eugenol is obtained by the usual methods in the isomerisation of the eugenol. The determination of the composition of this mixture offers some difficulty.

The known physical method, based on the viscosity of the mixture, suffers from the great disadvantage that the presence of small

quantities of other substances, water, terpenes, and so forth, renders it inaccurate.

The analysis of this mixture by means of the melting-point curve of a pair of solid derivatives affords a more accurate means of estimating the composition. Of the solid derivatives of eugenol and *iso*eugenol, the benzoates are the most simply prepared. Both isomerides are solid, crystalline substances which are insoluble in water and can readily be obtained quite pure and dry. Moreover, the melting points of the two derivatives are wide apart, and lie in a convenient range of temperature; eugenol benzoate, m. p. 69—70° (Tiemann and Kraas, *Ber.*, 1882, **15**, 2067); *iso*eugenol benzoate, m. p. 103—104° (Tiemann, *Ber.*, 1891, **24**, 2874). The melting-point curve is not quite a simple eutectic curve; the divergence, due probably to an unstable compound, is very slight, in the neighbourhood of the 50 per cent. mixture.

As contrasted with the long process of drying and fractionating the oil in a vacuum, essential when viscosity methods are used for determining the composition of this mixture, the solid, crystalline benzoates can be readily prepared from the crude oil and isolated so that the mixture will have the same relative composition as the original.

The crude oil, obtained in the isomerisation, is dissolved in pyridine, and treated with some 25 per cent. excess of benzoyl chloride. The major portion of the benzoates separates as a solid, and a further quantity on pouring the pyridine solution into dilute sulphuric acid. This solution is now extracted with ether to secure the last traces of the benzoates. To ensure intimate mixing of the two isomerides, the solid which separates is dissolved in the ether extract, from which, on evaporation of the ether, the solid benzoate mixture is obtained.

The pure benzoates required for plotting the melting-point curve were prepared by a similar treatment with benzoyl chloride of eugenol or *iso*eugenol dissolved in pyridine. The eugenol or *iso*eugenol benzoate was purified by repeated crystallisation from alcohol. Eugenol benzoate then melted at 69°, and *iso*eugenol benzoate at 103°. After sublimation in the vacuum of the Toepler pump, eugenol benzoate melted at 69·5° and *iso*eugenol benzoate at 104°. On resublimation, the melting points did not change.

Determination of the Fusion Points.—Following the method described in a previous paper (McKie, T., 1918, **113**, 799), a curve, followed from both pure eugenol and pure *iso*eugenol benzoates as starting point, was constructed. A well-marked eutectic point was observed at a temperature of 56·5°, corresponding with a composition of 25·5 per cent. of *iso*eugenol benzoate. But at tem-

peratures from 83—86°, and at compositions approximating to the equimolar mixture, there was a discontinuity in the curve. The curve is similar to the melting-point curves of phenol and carbamide, and of aniline and *p*-nitrophenol (Kremann, *Monatsh.*, 1906, **27**, 138), and the phenomenon here is, as in the above-mentioned pairs of substances, probably due to the formation of a compound which dissociates below its melting point. The range of disturbance of the curve is in this case very small, and does not invalidate the use of the melting point as a means of determining the composition of mixtures.

Eugenol benzoate. Grams.	*iso*Eugenol benzoate. Grams.	*iso*Eugenol benzoate. Per cent.	Melting point.
0·5689	—	—	69·5
,,	0·1083	16·0	64·0
,,	0·2322	29·0	65·8
,,	0·2677	32·0	69·4
,,	0·3063	35·0	72·5
0·7461	0·4979	40·0	79·7
,,	0·6479	46·5	82·7
,,	0·7919	51·5	83·6
0·4620	0·5588	54·9	{84·0
,,	,,	,,	{86·2
,,	0·5336	53·6	86·0
,,	0·6836	59·68	86·8
,,	0·9590	87·5	91·4
,,	1·638	78·0	98·2
,,	—	100·0	104
		(Eutectic 25·5	56·5)

My thanks are due to Professor Orton for direction and criticism in the above work.

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BANGOR. [*Received, March* 19*th*, 1921.]

LXXXVII.—*Piperitone. Part I. The Occurrence, Isolation, and Characterisation of Piperitone.*

By JOHN READ and HENRY GEORGE SMITH.

THE first recorded investigation of a eucalyptus oil is described in a publication by Cloëz, dealing with the leaf oil of *Eucalyptus globulus* (*Compt. rend.*, 1870, **70**, 687). Since that time the occurrence of about forty different constituents, consisting largely of terpenes and related substances, has been established in the essential oils of this distinctive Australian genus. It is noteworthy that

among this extensive series of substances only one exhibits ketonic properties. The constituent in question possesses a pronounced peppermint odour and taste, and is characteristic of the essential oils of a group of eucalypts known in Australia as "Peppermints." A species of this type, growing plentifully in the neighbourhood of Port Jackson, attracted attention soon after Governor Phillip's arrival in New South Wales in 1788, and the first eucalyptus oil to be distilled was obtained from its foliage and employed for medicinal purposes by Dr. White, Surgeon-General to the first settlement. "The name Peppermint Tree has been given to this plant by Mr. White on account of the very great resemblance between the essential oil drawn from its leaves and that obtained from the Peppermint (*Mentha piperita*) which grows in England. This oil was found by Mr. White to be much more efficacious in removing all cholicky complaints than that of the English Peppermint, which he attributes to its being less pungent and more aromatic" (White, "Journal of a Voyage to New South Wales," 1790, 227). The species of eucalypt which furnished this oil is now known as *Eucalyptus piperita*, and it is common in the Sydney district and the Blue Mountain Ranges of New South Wales.

Although the eucalyptus oils first produced in Australia for commercial purposes were distilled from species of the "Peppermint" group of eucalypts, yet for many years no attempt seems to have been made to distinguish the constituent imparting the characteristic odour to these oils. In the case of an oil said to be derived from *E. haemastoma*, the odour was at one time wrongly attributed to menthone (Schimmel, *Half-Yearly Report*, Leipzig, April, 1888, 20; Gildemeister and Hoffmann, "The Volatile Oils," 1900, 538). It was not until 1900 that the constituent in question was isolated by one of us in a fairly pure condition, with the aid of sodium hydrogen sulphite, from the oil of *E. dives* (*J. Proc. Roy. Soc. N.S. Wales*, 1900, **34**, 316). The odoriferous ketone thus obtained was shown to be distinct from menthone, but the molecular formula, $C_{10}H_{18}O$, originally assigned to it proved to be incorrect. Subsequently, the ketone was regarded as a new substance, and because of its association with the historically interesting species *E. piperita* it was named piperitone (Baker and Smith, "A Research on the Eucalypts," 1st ed., Sydney, 1902, 229).

It has been found that most constituents of eucalyptus oils increase in amount throughout a range of species until the attainment of a limiting value; in the case of piperitone, the maximum content is reached in the oil of *E. dives*. This species, which is also known as the "Broad-leaved Peppermint," is distributed over

an extensive area in New South Wales and Victoria, being in some districts the predominating species of eucalypt. The yield of oil from the green leaves and twigs of *E. dives* amounts to as much as 4 per cent., and when the distillation is continued for about eight hours the resulting oil often contains up to 40 per cent. of piperitone. It is thus apparent that piperitone could be obtained in Australia in almost unlimited quantity, particularly as the regrowth from the felled trees of *E. dives* is rapid and abundant, whilst the habitat is usually unsuitable for agricultural purposes. Piperitone occurs in the essential oils of the most recent species in the evolutionary sequence of the genus *Eucalyptus* (compare Baker and Smith, *op. cit.*), that is to say, in species which are common to south-eastern Australia and Tasmania. Further reference will be made in a later paper to the interesting fact that in every recorded case, with the exception of *E. apiculata*, piperitone occurs in eucalyptus oils in association with *l*-α-phellandrene: consequently, the leaves of the species concerned possess the characteristic "phellandrene venation." In most instances, piperitone seems also to be accompanied by the corresponding secondary alcohol, piperitol, which has been isolated from the essential oil of *E. radiata*. Cineole, it may be remarked, is not an abundant constituent of oils containing piperitone; thus in the case of *E. dives* it appears never to exceed about 8 per cent.

Recent investigations (Smith and Penfold, *J. Proc. Roy. Soc. N.S. Wales*, 1920, **54**, 40; Baker and Smith, *op. cit.*, 2nd ed., 1920, 390) have shown that piperitone is an unsaturated ketone possessing the molecular formula $C_{10}H_{16}O$. When isolated in the usual way, by fractional distillation under atmospheric pressure followed by treatment with sodium hydrogen sulphite solution, it is obtained as a colourless liquid which gradually turns yellow with lapse of time. Preparations made from the purified crystals of the bisulphite compound are optically inactive, but the piperitone regenerated from the filtrate usually exhibits a feeble lævorotation. This slight activity, which in most cases does not exceed $[\alpha]_D -1°$, may possibly be ascribed to the presence of small quantities of the lævorotatory aldehyde "cryptal"; the latter, being a characteristic constituent of the group of "Boxes," such as *E. hemiphloia*, may well persist to a slight degree in the essential oils of the more recently evolved groups of the genus (Baker and Smith, *op. cit.*, 1920, 386).

The interesting fact has also been disclosed (Smith and Penfold, *loc. cit.*) that by conducting the distillations under greatly diminished pressure it is possible to isolate the piperitone in a markedly active lævorotatory form. The magnitude of the rotation varied with different preparations; as an example, in a particular case the

observed value of $[\alpha]_D$ was $-42{\cdot}8°$. Other physical constants determined for the same specimen were as follows: d_4^{20} 0·9348; n_D^{20} 1·4837 and R_L 46·49; b. p. 106—107°/10 mm., 229—230°/760 mm. The corresponding values obtained for the optically inactive substance agreed closely with the above, but slight variations were noticeable with different preparations.

Up to the present, the chemical relationships of piperitone have only been submitted to a preliminary examination; the results, however, are of considerable interest, as revealing that *dl*-piperitone may readily be oxidised to thymol, by the aid of ferric chloride and acetic acid, or reduced to menthone by means of hydrogen in the presence of a nickel catalyst (Smith and Penfold, *loc. cit.*). Thus, although the information available has been insufficient to permit of a specific diagnosis, the structure of a *p*-menthen-3-one has been assigned to piperitone. The formation of a bimolecular ketone by reducing *dl*-piperitone with sodium amalgam in a moist ether–alcohol solution provides the best method yet described for its recognition and characterisation: this compound, $C_{20}H_{34}O_2$, melts at 149—150°, and its dioxime, $C_{20}H_{36}O_2N_2$, at 245° (Baker and Smith, *op. cit.*, 1920, 393). No definite brominated derivative has yet been prepared.

dl-Piperitone forms both an oxime (m. p. 110—111°) and a hydroxylamino-oxime (m. p. 169—170°). The latter derivative results when an excess of hydroxylamine is used, and from the reactions described below the hydroxylamino-group appears to be attached to a tertiary carbon atom (Harries, *Ber.*, 1899, **31**, 2896).

dl-Piperitonesemicarbazone, when prepared by the method described below, melts at 219—220°, and hence is not particularly characteristic of the ketone, since the Δ^1-*p*-menthen-3-one described by Wallach (*Annalen*, 1908, **362**, 272) yields a semicarbazone having almost the same melting point (224—226°). There are differences, however, in ease of formation and solubility.

Undoubtedly the most characteristic derivative of piperitone yet prepared is benzylidene-*dl*-piperitone, also described in this paper and corresponding with the molecular formula $C_{10}H_{14}O\colon CHPh$. This is formed with striking ease by the interaction of piperitone and benzaldehyde in the presence of alcoholic sodium ethoxide, and is readily obtained in the form of beautiful, well-developed crystals melting at 61°; the compound is thus eminently adapted to the recognition of piperitone and its differentiation from related ketones. The preparation of this derivative may be advanced as a convincing proof of the non-identity of piperitone with any of the menthenones hitherto described, and the unusual facility with which it is formed is important on structural grounds.

We reserve the very interesting question of the constitution of piperitone for discussion in a later communication. Further, in view of the great degree of importance, both scientific and economic, which appears to us to attach to this substance, we propose to undertake a systematic study of piperitone and its derivatives. Even in the light of the data now available, the opinion may perhaps be expressed that this eucalyptus ketone, by virtue of its chemical nature and its plentiful occurrence, may eventually attain a position of importance intermediate between menthone and camphor.

EXPERIMENTAL.

dl-*Piperitone*.

The piperitone utilised in the following work was isolated from the essential oil of *E. dives* in the manner already indicated, except that it was found advantageous to use normal sodium sulphite in place of the bisulphite. Since the preliminary distillations were carried out under atmospheric pressure, the product exhibited only feeble optical activity. Some of the physical characteristics of a typical preparation were determined, with the following results: $[\alpha]_D$ −0·27°; n_D^{20} 1·4843; b. p. 128·5°/25 mm. It is to be noted, however, that accurate determinations of the physical constants of chemically and optically pure piperitone have yet to be made.

dl-*Piperitonehydroxylamino-oxime*, $HON:C_{10}H_{17}\cdot NH\cdot OH$.

To a solution of *dl*-piperitone (6 grams) in three times its volume of absolute alcohol was added a solution of potassium hydroxide (6 grams) in water (3 c.c.). The mixture was heated to 70° and treated with a solution of hydroxylamine hydrochloride (6 grams) in water (6 c.c.). After maintaining at 70—80° for ten minutes, the liquid was cooled, poured into about five times its volume of water, and left for twelve hours. The resulting mass of crystals was separated, dried on porous plate, washed with ether, and finally crystallised from alcohol containing a little ether, in which latter solvent it was sparingly soluble. The substance formed small, colourless needles, which melted at 169—170° and showed no tendency to recrystallise on cooling. It reduced Fehling's solution readily when heated, and gave a blue coloration when boiled in alcoholic solution with mercuric oxide. A solution in a mixture of alcohol and chloroform gave a bright bluish-green colour with a trace of bromine, changing to emerald-green upon the addition of a little more of the halogen (Found: C=59·7; H=10·2. $C_{10}H_{20}O_2N_2$ requires C=59·95; H=10·07 per cent.).

dl-*Piperitoneoxime*, $C_{10}H_{16}$:NOH.

When the above method was applied, using exactly one molecular proportion of hydroxylamine hydrochloride, the normal oxime resulted. It was readily soluble in ether, but only moderately soluble in light petroleum, from which solvent it was deposited in the form of magnificent colourless prisms, exhibiting high transparency and lustre. The oxime melted at 110—111°, and recrystallised immediately on cooling. It gave none of the colour reactions exhibited by the hydroxylamino-oxime (Found: C=71·2; H=10·1. $C_{10}H_{17}ON$ requires C=71·79; H=10·25 per cent.).

dl-*Piperitonesemicarbazone*, $C_{10}H_{16}$:N·NH·CO·NH_2.

dl-Piperitone was mixed with an equal volume of a cold saturated solution of semicarbazide hydrochloride, and just sufficient alcohol to render the liquid clear. Reaction occurred with comparative ease, and a copious separation of colourless crystals took place within the course of a few hours. After one recrystallisation from boiling absolute alcohol, in which the substance was only moderately soluble, minute, colourless crystals were obtained melting at 219—220° (Found: N=20·2. $C_{11}H_{19}ON_3$ requires N=20·1 per cent.).

Benzylidene-dl-*piperitone*, $C_{10}H_{14}$O:CHPh.

In the original preparation of benzylidenepiperitone, the ketone was dissolved in about twice its volume of absolute alcohol, together with one molecular proportion of benzaldehyde. Rather more than one equivalent weight of sodium, freshly dissolved in about ten times its weight of absolute alcohol, was then added to the cooled solution. Rapid darkening occurred, attended by an appreciable evolution of heat. The smell of benzaldehyde disappeared within a few hours, and after twenty-four hours a considerable amount of crystalline material had separated from the dark brown liquid. When the mixture had stood for three days in a stoppered flask, it was poured into ice-water and extracted with ether. The dried ethereal extract, when distilled from the water-bath, yielded a viscous, brown liquid residue which could not be induced to crystallise. Upon distilling the product under diminished pressure, very little distillate could be collected below 245°/25 mm., but from this temperature to about 258°/25 mm. a limpid, pale yellow liquid passed over, which on cooling became viscous. A further fraction, collected up to 350°/25 mm., distilled as a very viscous, orange-coloured liquid, solidifying on cooling to a transparent, vitreous mass. The residue, which contained the bulk of the material,

solidified to a brittle, dark brown resin. It proved impossible to obtain any crystalline product from the second fraction or the residue, but after considerable difficulty the fraction, b. p. 245—258°/25 mm., was induced to deposit crystalline material by treatment with suitable organic solvents, in all of which it dissolved with great ease. The weight of this fraction amounted to about one-half the weight of the piperitone used, and the yield of crystalline material to about 20 per cent. of the weight of the ketone.

The above procedure was modified in various ways, in an attempt to reduce the loss of material in the form of resin. In all cases the reaction appeared to proceed so readily that eventually the proportion of sodium was lessened: with only two-thirds of the equivalent amount of sodium, the yield of crystalline product was doubled, and with still less sodium, the results were even more favourable. The best conditions seemed to be attained by using about one-quarter of an equivalent weight of sodium. In this case, no deposition of solid material occurred from the alcoholic reaction mixture.

An example of the ultimate method adopted may now be given: 25 grams of piperitone were mixed with the requisite amount (17·5 grams) of benzaldehyde, and dissolved in absolute alcohol (60 c.c.). To the cold solution was added rapidly a cold solution of sodium (1 gram) in absolute alcohol (50 c.c.). The mixture was kept in a stoppered flask for three or four days; it was then poured into a slight excess of cold and very dilute sulphuric acid and extracted with ether. The brown residue which was left after evaporation on the water-bath crystallised almost completely when inoculated at the ordinary temperature with crystalline material from a preceding operation. Upon distillation, it yielded 26 grams of a pale yellow, highly refracting oil, b. p. 245—258°/25 mm., and this, upon inoculation, solidified to a hard, pale yellow, crystalline mass.

In purifying the last-named distillate, it was found advantageous to mix it in the original liquid form with a little warm methylated spirit, or, preferably, methyl alcohol: the resulting solution, when cooled and seeded, yielded a crystalline separation capable of ready collection and washing. The melting point of material prepared in this way was 59—60°. After one recrystallisation from methyl alcohol, the substance melted at 61°, and further recrystallisations had no effect upon the melting point. The results of analysis corresponded with a monobenzylidene derivative of piperitone (Found: C=85·1; H=8·4. $C_{17}H_{20}O$ requires C=84·94; H=8·39 per cent.).

In none of the cases recorded could either benzaldehyde or piperitone be detected among the products of reaction. The resinous material which is invariably produced to some extent can therefore

scarcely contain a dibenzylidene derivative, such as that described by Wallach for Δ^4-*p*-menthen-3-one (*Annalen*, 1899, **305**, 273). In the preparation just quoted, the amount of sodium used was about one-quarter of the equivalent quantity, and it may be mentioned that 25 grams of piperitone, when treated in a similar way with only one-half this proportion of sodium (0·5 gram), still yielded 23 grams of crystalline distillate. In this case, however, a small amount of benzaldehyde remained unchanged at the end of the reaction.

FIG. 1.

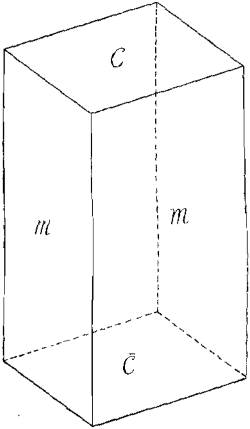
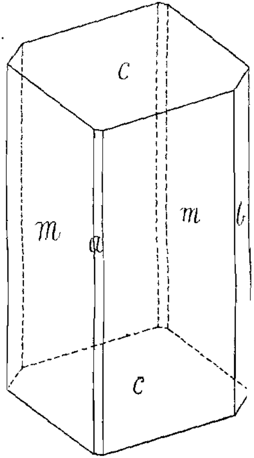


FIG. 2.

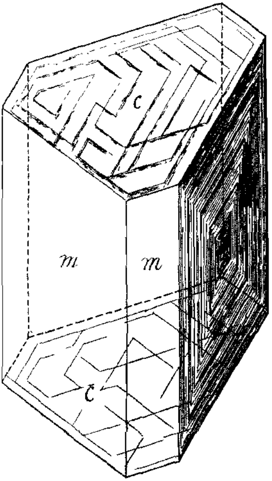


Benzylidene-*dl*-piperitone is a pale yellow solid which retains it colour fully after repeated crystallisation. When kept for severa months in a glass vessel exposed to the light, the surface laye undergoes a change, becoming pasty and deepening in colour. Th substance dissolves readily in the cold in all the ordinary organi solvents, including light petroleum, but it is almost insoluble i water. It has a marked tendency to form supersaturated solution In view of the slight optical activity of the preparations of piperitor used in this work, it is interesting to note that a 5 per cent. alcohol solution of a specimen of the benzylidene derivative which had be

prepared without being distilled was optically inactive when examined in a 2-dcm. tube in sodium light. It seems likely, therefore, that the activity of the original piperitone was due to contamination with small amounts of a lævorotatory impurity.

When allowed to crystallise slowly from methyl alcohol or ethyl alcohol, benzylidene-*dl*-piperitone is deposited in the form of magnificent pale yellow prisms, which may attain a considerable

FIG. 3.



size and exhibit very pronounced lustre and transparency. The results are appended of a goniometric examination of these crystals, for which we are indebted to Miss Marie Bentivoglio, B.Sc., of the Department of Geology, University of Sydney:

"The crystals observed were divided chiefly according to habit, one group exhibiting crystals of distinctly prismatic habit, the other, larger, group including crystals of tabular habit. The forms developed on crystals of the former group are: *a* (100), *b* (010), *c* (001), *m* (110). The primary prism is always well developed (Figs. 1 and 2), while it is only occasionally that the clino-pinacoid, generally a narrow face, assumes the form shown in Fig. 3. In

such instances, however, hour-glass structure (due to the mode of growth of the crystal) is prominent. The basal pinacoid is generally smooth, but at times assumes the rough and rather scaly appearance of a solution surface (Fig. 3). An indistinct cleavage was observed parallel to *m* (110).

"Crystallographic results given are only complete in so far as the data were available.

"*Crystal System.*—Monoclinic, holohedral.

"*Axial Ratios.*—$a : b : c = 0{\cdot}9331 : 1 : —$. $\beta = 72° 36'$.

Angle.	No. of measurements.	Limits.	Observed.	Calculated.
mm = 1̄10 : 110	15	83° 02′— 83° 32′	83° 18′	83° 18′
mm = 110 : 1̄10	15	96° 20′— 96 52′	96° 43′	96° 42′
am = 100 : 110	8	41° 21′— 41° 52′	41° 38′	41° 39′
mb = 110 : 010	20	48° 04′— 48° 36′	48° 21′	48° 21′
ac = 100 : 001	6	107° 15′—107° 40′	107° 24′	107° 24′
bc = 010 : 001	6	89° 49′— 90° 11′	89° 54′	90° 00′

"The crystals of the second group are not well developed; some faces are rounded, and others strongly striated. Moreover, there are not sufficient measurements available to correlate them definitely with the crystals of the first group. It is to be hoped that further crops will yield more satisfactory crystals, so that their relation to that group may be determined."

Benzylidene-*dl*-piperitone formed a dark red solution when dissolved in a 15 per cent. solution of hydrogen bromide in glacial acetic acid, but after the mixture had stood for several hours most of the original compound was recovered by pouring it into water. Stronger solutions, when kept for longer periods, deposited crystals which probably denoted the formation of a hydrobromide. The benzylidene derivative reacted readily with hydroxylamine.

Benzylidene-dl-*piperitoneoxime*, $HON{:}C_{10}H_{14}{:}CHPh,H_2O$.

The benzylidene derivative (5 grams) was dissolved in five times its weight of absolute alcohol, and the same amount of hydroxylamine hydrochloride was dissolved in its own weight of water The hot solutions were mixed and then treated with sodium hydroxide (5 grams) dissolved in water (2·5 c.c.). After standing overnight, the product of the reaction was poured into cold water. The resulting precipitate, after collection and drying in the air, was readily soluble in organic solvents. Owing to the persistence with which it retained water, it was most conveniently crystallised with the aid of methyl alcohol, from which solvent it was deposited after several recrystallisations in the form of rosettes of small, colourless needles. Upon exposure to the atmosphere, the substance graduall

turned yellow, but the colour was instantly removed by moistening with methyl alcohol. When heated slowly, it softened at about 99°, and after being allowed to resolidify melted at 130—131·5°. It proved to contain one molecular proportion of combined water (Found: N=5·7, after drying at 100°. Loss of weight at 100°= 6·6. $C_{17}H_{21}ON$ requires N=5·5 per cent.; $C_{17}H_{21}ON,H_2O$ requires H_2O=6·6 per cent.).

The bimolecular ketone of piperitone failed to react with benzaldehyde and sodium ethoxide under any of the conditions described.

The investigation is being continued.

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LXXXVIII.—*Studies in the Camphane Series. Part XXXIX.* p-*Aminophenylaminocamphor* (*Camphoryl*-p-*phenylenediamine*).

By MARTIN ONSLOW FORSTER and WILLIAM BRISTOW SAVILLE.

REQUIRING an optically active diazotisable amine for the purpose of another investigation, we have examined various methods of preparing *p-aminophenylaminocamphor*, $C_8H_{14}<\begin{matrix}CH\cdot NH\cdot C_6H_4\cdot NH_2\\ CO\end{matrix}$ (I.), the camphoryl derivative of *p*-phenylenediamine. The common process for obtaining phenylaminocamphor and its products of substitution would indicate the reduction of *p*-nitrophenyliminocamphor as the obvious source of *p*-aminophenylaminocamphor, but in spite of the readiness with which aromatic amines undergo condensation with camphorquinone (Forster and Thornley, T., 1909, **95**, 942; Forster and Spinner, T., 1919, **115**, 889; B. K. Singh and collaborators, T., 1919, **115**, 566, and 1920, **117**, 980, 1599), the nitroanilines were found to be exceptions, and a nitrophenyliminocamphor has not been hitherto obtainable. Incidentally, the reason for this has now come to light in consequence of the indirect formation of *o*- and *p*-nitrophenyliminocamphor, both being hydrolysed to camphorquinone and the respective nitroaniline with a facility which explains the failure to produce them by direct condensation.

The formation of these compounds has arisen from examining the action of nitric acid on the nitrosoamine of phenylaminocamphor. Under conditions which leave this base unchanged, the nitrosoamine

is readily nitrated, a difference recalling the behaviour of diphenylamine and its nitrosoamine as described by H. and P. Ryan (*Proc. Roy. Irish Acad.*, 1918, **34**, [*B*], 194). A mixture of *o*- and *p*-nitrophenylnitrosoaminocamphor (III) is thus produced, and from these two substances the respective *o*- and *p*-nitrophenyliminocamphors (IV) have been obtained by the action of alcoholic alkali hydroxide:

$$C_8H_{14}<\begin{matrix}CH\cdot N(NO)\cdot C_6H_5\\|\\CO\end{matrix} \text{ (II.)} \longrightarrow C_8H_{14}<\begin{matrix}CH\cdot N(NO)\cdot C_6H_4\cdot NO_2\\|\\CO\end{matrix} \text{ (III.)}$$

$$\longrightarrow C_8H_{14}<\begin{matrix}C{:}N\cdot C_6H_4\cdot NO_2\\|\\CO\end{matrix} \text{ (IV.)}.$$

Although belonging to the class characterised by the highest recorded optical activity, their molecular rotatory power, 313° and 1065°, respectively, is unimportant when compared with that of allied substances, thus offering an example of the negative effect produced by the nitro-group (compare Giemsa and Halberkann, *Ber.*, 1920, **53**, [*B*], 732).

When the nitrosoamine itself is treated with alcoholic alkali hydroxide, two changes take place, one analogous to the above, and another, which prepouderates, leading to the isomeric oxime of *N*-phenylcamphorimide:

$$C_8H_{14}<\begin{matrix}C{:}N\cdot C_6H_5\\|\\CO\end{matrix} \longleftarrow \text{II} \longrightarrow C_8H_{14}<\begin{matrix}C({:}NOH)\\CO\end{matrix}>N\cdot C_6H_5 \text{ (V.)}.$$

This transformation recalls that described by Lowry (T., 1898, **73**, 1000), who showed that the isomeric change of nitrocamphor, first observed by Cazeneuve, leads to the oxime of camphoric anhydride; in the case under discussion, this rearrangement must be preceded by transference of the nitroso-group from nitrogen to carbon.

Although sluggish in action with nitric acid, phenylaminocamphor readily takes part in the process of coupling with diazonium salts, when *p*-azo-compounds are produced. These are intensely coloured, but in common with other derivatives of phenylaminocamphor, they do not display remarkable optical activity. The sulphonic acid of benzeneazophenylaminocamphor (VI) has the property of separating from hot aqueous solution in colloidal form which becomes deflocculated in contact with crystals, produced by kneading the sludge with alcohol. It is this compound which first led to *p*-aminophenylaminocamphor by reduction,

$$C_8H_{14}<\begin{matrix}CH\cdot NH\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot SO_3H\\|\\CO\end{matrix} \text{ (VI.)} \longrightarrow$$

$$C_8H_{14}<\begin{matrix}CH\cdot NH\cdot C_6H_4\cdot NH_2\\|\\CO\end{matrix},$$

but the base is more conveniently prepared from its acetyl deriv-

ative, obtained by reducing acetylaminophenyliminocamphor, the product of condensing camphorquinone with *p*-aminoacetanilide (Forster and Spinner, *loc. cit.*). Incidentally, this origin of the substance establishes the position entered by the benzeneazo-group on coupling.

An unexpected irregularity has presented itself in connexion with the optical activity of camphorylaminophenyliminocamphor (VII), the product of condensing camphorquinone with *p*-aminophenylaminocamphor. Comparison of *p*-phenylenebisiminocamphor (VIII), phenyliminocamphor, and phenylaminocamphor revealed the remarkable effect of unsaturation and of conjugated linkages on optical activity (Forster and Thornley, *loc. cit.*), and the same point has been emphasised by B. K. Singh (*loc. cit.*), notably with reference to 1 : 4-naphthylenebisiminocamphor. From all these results it was to be expected that the molecular rotation of camphorylaminophenyliminocamphor would be less than that of *p*-phenylenebisiminocamphor, but it is greater :

(VII.) $C_8H_{14}<\begin{matrix}C{:}N\cdot C_6H_4\cdot NH\cdot CH \\ CO \qquad\qquad\qquad OC\end{matrix}>C_8H_{14}$ $[M]_D$ 6663° (chloroform) 8079 (pyridine)

(VIII.) $C_8H_{14}<\begin{matrix}C{:}N\cdot C_6H_4\cdot N{:}C \\ CO \qquad\qquad OC\end{matrix}>C_8H_{14}$ $[M]_D$ 6096° (chloroform) 6173 (pyridine)

On the other hand, camphorylaminonaphthyliminocamphor,

(IX.) $C_8H_{14}<\begin{matrix}C{:}N\cdot C_{10}H_6\cdot NH\cdot CH \\ CO \qquad\qquad\qquad OC\end{matrix}>C_8H_{14}$, $[M]_D$ 7688° (chloroform) 9261 (pyridine),

displays molecular rotation which, although greater than that of the foregoing phenyl derivative, is considerably below the constant recorded for 1 : 4-naphthylenebisiminocamphor.

EXPERIMENTAL.

Nitration of Phenylaminocamphor and the Nitroso-derivative.

Phenylaminocamphor develops with concentrated nitric acid a characteristic, intense cherry-red coloration, fading to pale brown in a few hours. The *hydrochloride* melts and evolves gas at 199° (Found : N=4·98. $C_{16}H_{21}ON,HCl$ requires N=5·01 per cent.). The *acetyl* derivative melts at 104° (Found : N=4·96. $C_{18}H_{23}O_2N$ requires N=4·91 per cent.); a solution containing 0·2003 gram in chloroform diluted to 25 c.c. gave α_D − 0° 17′ in a 1-dcm. tube, whence $[\alpha]_D$ − 35·3°.

Attempts to prepare nitrophenylaminocamphor by direct action of nitric acid failed, the base remaining unchanged when treated in acetic acid with one molecular proportion of the free mineral acid, and also in sulphuric acid to which finely powdered sodium nitrate

was added. A *dinitro*-derivative, $C_{16}H_{19}O_5N_3$, was produced, however, on adding nitric acid (10 c.c.) to phenylaminocamphor (5 grams) dissolved in glacial acetic acid (10 c.c.), separating with development of heat which could not readily be controlled; colour changes from purple through green to brown accompanied the appearance of orange crystals which filled the liquid. After being washed with glacial acetic acid and recrystallised from boiling alcohol, it melts at 191°, but if recrystallised from acetone, at 204° (Found: C=58·03; H=5·90; N=12·64. $C_{16}H_{19}O_5N_3$ requires C=57·65; H=5·70; N=12·61 per cent.); a solution containing 0·5006 gram in chloroform diluted to 25 c.c. gave α_D − 2° 25′ in a 1-dcm. tube, whence $[\alpha]_D$ − 120·7°.

Phenylnitrosoaminocamphor (Forster and Thornley, *loc. cit.*) was prepared by dissolving phenylaminocamphor (20 grams) in 30 per cent. sulphuric acid (50 c.c.), mixing with alcohol (50 c.c.), and adding sodium nitrite (7 grams) in water (25 c.c.) and alcohol (25 c.c.) slowly, with constant stirring and cooling. The crystalline precipitate was washed once with 50 per cent. alcohol and then thoroughly with water, otherwise the product darkens on drying The nitrosoamine crystallises from alcohol in minute, almost colourless needles, faintly yellow when viewed in bulk, and melts at 74° not 80—81° as previously stated (Found: C=70·65; H=7·46 N=10·26. $C_{16}H_{20}O_2N_2$ requires C=70·59; H=7·35; N=10·2[illegible] per cent.). A solution containing 1·0250 grams in chloroform dilute[illegible] to 25 c.c. gave α_D −0° 9′ in a 1-dcm. tube when examined immediately reaching a maximum of 0° 16′ within two hours; thus the $[\alpha]$ changes from −3·6° to +6·5°. Even when purified chloroform i[illegible] used, the solution becomes deep cherry-red, and on evaporatio[illegible] leaves a residue from which camphorquinone volatilises.

Conversion into the Oxime of N-*Phenylcamphorimide* (V).—Th[illegible] nitrosoamine (5 grams) was added in small portions to a solutio[illegible] of potassium hydroxide (1·3 grams) in water (2 grams) mixed wit[illegible] alcohol (8 c.c.); slight rise of temperature occurred, but gas w[illegible] not liberated and the orange coloration at first developed quick[illegible] faded. One molecular proportion of alkali is necessary for co[illegible] plete action. On dilution with water (about 40 c.c.), the liqu[illegible] became turbid, and after twelve hours phenyliminocamphor (0[illegible] gram) was filtered, neutralisation with acetic acid then produci[illegible] a voluminous white precipitate. The product separated on aqueo[illegible] dilution of the solution in cold alcohol, which dissolves it freely; formed a spongy mass of minute, thread-like needles, and w[illegible] recrystallised by carefully adding ethyl acetate to a suspension hot petroleum (Found: C=70·55; H=7·49; N=10·07. $C_{16}H_{20}O_2$[illegible] requires C=70·59; H=7·35; N=10·29 per cent.). It melts

155°, and the alcoholic solution develops an intense red coloration with ferric chloride. When the solution in concentrated hydrochloric acid is boiled uuder reflux during two hours, crystals of camphoric acid separate on cooling, aniline and hydroxylamine being found in the filtrate. A solution containing 0·4998 gram in chloroform diluted to 25 c.c. gave α_D 4° 57′ in a 1-dcm. tube, whence $[\alpha]_D$ 247·6°. The *benzoyl* derivative melts at 177° after crystallisation from alcohol (Found: C=73·36; H=6·48. $C_{23}H_{24}O_3N_2$ requires C=73·40; H=6·38 per cent.). A solution containing 0·4287 gram in chloroform diluted to 25 c.c. gave α_D 2° 6′ in a 1-dcm. tube, whence $[\alpha]_D$ 122·4°.

o- *and* p-*Nitrophenylnitrosoaminocamphor* (III).—The nitrosoamine (20 grams), dissolved in glacial acetic acid (70 c.c.), was treated with a mixture of 70 per cent. nitric acid (7 grams) and glacial acetic acid (10 c.c.), the mixture being immediately cooled and stirred. Yellow crystals quickly appeared, aud after one hour the thick paste was filtered, washed twice with glacial acetic acid, then with 50 per cent. acid, and finally with water until the filtrate was neutral. The product weighed 20 grams, and after being extracted during eight hours with light petroleum in a Soxhlet apparatus, was recrystallised from hot acetone, the p-*nitrophenylnitrosoaminocamphor* separating in pale straw-coloured needles which melt and decompose at 158°; it is sparingly soluble in boiling alcohol (Found: C=60·11; H=6·07; N=13·09. $C_{16}H_{19}O_4N_3$ requires C=60·56; H=5·99; N=13·25 per cent.). A solution containing 0·5004 gram in chloroform diluted to 25 c.c. gave α_D 0° 42′ in a 1-dcm. tube, whence $[\alpha]_D$ 35·0°. o-*Nitrophenylnitrosoaminocamphor* was found in the petroleum extract and the acetone mother-liquor. Successive dilution of the latter with water gave ultimately a fraction almost free from the isomeride; it was then dissolved in the necessary amount of hot benzene, precipitated with an equal quantity of warm petroleum, and finally recrystallised from hot alcohol. It separates in minute, transparent, straw-coloured prisms, and melts at 122° with decomposition (Found: C=60·80; H=6·09; N=13·08. $C_{16}H_{19}O_4N_3$ requires C=60·56; H=5·99; N=13·25 per cent.). A solution containing 1·0005 grams in chloroform diluted to 25 c.c. gave α_D 4° 36′ in a 1-dcm. tube, whence $[\alpha]_D$ 114·9°. Mixtures of the two isomerides melt indefinitely at temperatures which vary between 122° and 158°, according to the proportion of each. The most convenient means of separating the *ortho*-compound from such mixtures is to extract them with an amount of cold benzene insufficient to dissolve the *para*-derivative, precipitating the more soluble isomeride with an equal volume of cold petroleum.

o- *and* p-*Nitrophenyliminocamphor* (IV).—*p*-Nitrophenylnitrosoaminocamphor (5 grams) was added in small portions to alcohol in which sodium (0·5 gram) had been dissolved. The liquid became orange and evolved nitrous fumes while yellow crystals (1·3 grams) separated. After recrystallisation from alcohol, p-*nitrophenyliminocamphor* melts at 136° (Found: C=66·85; H=6·23; N=9·73. $C_{16}H_{18}O_3N_2$ requires C=67·13; H=6·29; N=9·79 per cent.). A solution containing 1·0001 grams in chloroform diluted to 25 c.c. gave α_D 14° 54′ in a 1-dcm. tube, whence $[\alpha]_D$ 372·4°. The original filtrate from this compound contained *p*-nitroaniline, which is also formed when the purified substance is dissolved in glacial acetic acid or heated in alcohol with dilute sulphuric acid, camphorquinone being regenerated. In consequence of this behaviour the preparation was modified by adding *p*-nitrophenylnitrosoaminocamphor (4·5 grams) to benzene (10 c.c.) surmounting a solution of potassium hydroxide (1·3 grams) in water (5 c.c.) and alcohol (5 c.c.), in a separating funnel. The aqueous layer became brown, and when nitrous fumes were no longer liberated the benzene was washed and allowed to evaporate, depositing 2·8 grams; but the aqueous alcohol contained camphorquinone and *p*-nitroaniline. o-*Nitrophenyliminocamphor* was obtained from *o*-nitrophenylnitrosoaminocamphor by similar procedure, and crystallised from alcohol in lustrous yellow plates melting at 142° (Found: C=67·04; H=6·48; N=9·77. $C_{16}H_{18}O_3N_2$ requires C=67·13; H=6·29; N=9·79 per cent.). A solution containing 0·2057 gram in chloroform diluted to 25 c.c. gave α_D 0° 54′ in a 1-dcm. tube, whence $[\alpha]_D$ 109·4°. It is not hydrolysed quite so readily as the *para*-compound by acetic acid. A mixture of the two isomerides in equal parts melts sharply at 112°, and recrystallisation from alcohol does not change the melting point. The substances were first obtained in this form, and until the presence of *o*-nitrophenylnitrosoaminocamphor in the product of nitrating phenylnitrosoaminocamphor was recognised, it was believed that the molecular mixture represented an individual substance; hydrolysis yields a mixture of the nitroanilines, however, whilst the rotation amounted to 237·8°, approximating to the mean of the values recorded above.

p-*Aminophenylaminocamphor* (*Camphoryl*-p-*phenylenediamine*), (I).

The most convenient source of this base is the *acetyl* derivative, obtained by adding zinc dust to an alcoholic solution of *p*-acetylaminophenyliminocamphor until this is colourless, when it was precipitated from the filtrate by water and recrystallised twice from alcohol, then melting at 167° (Found: C=71·86; H=8·08.

$C_{18}H_{24}O_2N_2$ requires C=72·00; H=8·00 per cent.). A solution containing 0·9994 gram in chloroform diluted to 25 c.c. gave α_D 3° 30′ in a 1-dcm. tube, whence $[\alpha]_D$ 87·5°. On heating the compound (20 grams) with alcohol (100 c.c.) and concentrated hydrochloric acid (100 c.c.) during three hours under reflux, the liquid when cold was filled with lustrous, colourless needles consisting of the *dihydrochloride* of the base (Found: N=8·73; Cl=21·50. $C_{16}H_{22}ON_2,2HCl$ requires N=8·46; Cl=21·45 per cent.). The salt becomes pale brown at about 150°, but does not melt and evolve gas until 190°; a solution in water rapidly becomes brown when heated. The *base* separated as a sticky mass, rapidly becoming hard, when ammonia was added to the aqueous dihydrochloride; the air-dried substance (12 grams) was dissolved in warm benzene (20 c.c.) and precipitated in pale brown crystals by adding petroleum (20 c.c.); after a similar recrystallisation it melts at 106° (Found: C=74·68; H=8·55; N=10·80. $C_{16}H_{22}ON_2$ requires C=74·41; H=8·52; N=10·85 per cent.). A solution containing 0·4994 gram in chloroform diluted to 25 c.c. gave α_D 1° 54′ in a 1-dcm. tube, whence $[\alpha]_D$ 95·1°. The base is noticeably sensitive to oxygen, especially when dissolved. The *benzoyl* derivative melts at 206° after crystallisation from alcohol (Found: N=7·79. $C_{23}H_{26}O_2N_2$ requires N=7·73 per cent.).

Camphorylaminophenyliminocamphor (VII), prepared by heating aminophenylaminocamphor and camphorquinone in alcohol, is very sparingly soluble in that medium; it was therefore purified by adding alcohol to the solution in chloroform, slow evaporation of the latter leading to deposition of dense, spherical nodules, the crystals melting at 234° (Found: N=7·09. $C_{26}H_{34}O_2N_2$ requires N=6·90 per cent.). A solution containing 0·0655 gram in chloroform diluted to 25 c.c. gave α_D 4° 18′ in a 1-dcm. tube, whence $[\alpha]_D$ 1641°; a similar solution in pyridine containing 0·0603 gram gave α_D 4° 48′, whence $[\alpha]_D$ 1990°. These correspond to $[M]_D$ 6663° and 8079°, respectively.

Derivatives of p-*Benzeneazophenylaminocamphor.*

These compounds are produced very readily by coupling diazonium salts with phenylaminocamphor. On adding the solution prepared from aniline (0·9 gram) diazotised in hydrochloric acid (4 grams) to the base (2·4 grams) dissolved in alcohol (30 grams), there developed a carmine coloration which rapidly became very intense, garnet-coloured crystals beginning to separate within one hour. Melting at 169°, the product is identical with *p*-benzeneazophenylaminocamphor prepared by reducing the condensation product from camphorquinone and *p*-aminoazobenzene (Forster and Spinner,

T., 1919, **115**, 894), thus determining the *para*-position of the entrant azo-group. A solution containing 0·0701 gram in chloroform diluted to 25 c.c. gave α_D 0° 20′ in a 1-dcm. tube, whence $[\alpha]_D$ 118·8°. It is probable that the first stage in the coupling process is the diazoamino-compound, $C_8H_{14}<\begin{matrix}CH\cdot N(N{:}N\cdot C_6H_5)\cdot C_6H_5\\ |\\ CO\end{matrix}$, because on one occasion there was produced a substance crystallising from warm alcohol in brown needles melting at 134°, and changing into the garnet-red azo-compound when an attempt was made to crystallise it from the boiling solvent.

p-*Nitrobenzeneazophenylaminocamphor* was prepared by adding *p*-nitroaniline diazotised in hydrochloric and acetic acids to phenylaminocamphor dissolved in a similar mixture, an intense carmine coloration appearing immediately; sticky lumps separated and became brownish-red when treated with melting ice, changing to a red powder on trituration with alcohol. The product was then easily filtered, and crystallised from much boiling alcohol in vermilion leaflets with gold reflex; it melts at 207—209° (Found: N=14·32. $C_{22}H_{24}O_3N_4$ requires N=14·28 per cent.). It dissolves much more readily in boiling acetone, of which 45 grams are required by six, and separates in dark red prisms; it resembles the parent compound in developing a rich carmine coloration when hydrochloric acid is added to an alcoholic solution.

p-*Sulphobenzeneazophenylaminocamphor* (VI) separated as a deep crimson, colloidal mass when diazotised sulphanilic acid was added to a solution of phenylaminocamphor in acetic acid, and became crystalline on treatment with alcohol; after recrystallisation from the boiling solvent, it forms deep-red needles which become purple in sunlight and intumesce at 235° (Found: C=60·47; H=6·65; N=9·01. $C_{22}H_{25}O_4N_3S,C_2H_6O$ requires C=60·88; H=6·55; N=8·88 per cent.). The substance is sparingly soluble in boiling water, 0·5 gram requiring 200 c.c., and as it cools, the pale, reddish-brown solution becomes much darker before being filled with a deep brown gelatinous mass; this does not crystallise spontaneously, but when treated with alcohol or sown with a crystalline specimen it rapidly becomes deflocculated in the form of lustrous, reddish-purple needles. The portion undissolved, even after continued treatment with boiling water, is dark purple and crystalline, intumescing at 263° (Found: C=61·57; H=5·90; N=9·79. $C_{22}H_{25}O_4N_3S$ requires C=61·82; H=5·85; N=9·83 per cent.). The dry substance has a sternutatory effect, and an alcoholic solution develops an intense carmine coloration with hydrochloric acid. Reduction with zinc dust in alkaline solution gave rise to *p*-aminophenylaminocamphor.

pp-*Diphenylenebisazophenylaminocamphor*,

$$C_8H_{14}<\begin{matrix}CH\cdot NH\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot NH\cdot CH \\ | \\ CO\end{matrix}\quad\begin{matrix} | \\ OC-\end{matrix}>C_8H_{14},$$

prepared by adding tetrazotised benzidine (0·9 gram) to phenylaminocamphor (2·4 grams) in acetic and hydrochloric acids, separates as a brown precipitate on adding water to the deep purple liquid. After removing impurities which are readily soluble in hot alcohol, the bisazo-compound remains as a pale brown powder, and when crystallised from much boiling alcohol melts at 244° (Found: C=75·65; H=7·07; N=11·90. $C_{44}H_{48}O_2N_6$ requires C=76·30; H=6·93; N=12·14 per cent.). The colour developed in an alcoholic solution by hydrochloric acid is intense blue.

4-*Amino*-1-*naphthylaminocamphor* (*Camphoryl*-1 : 4-*naphthylenediamine*), $C_8H_{14}<\begin{matrix}CH\cdot NH\cdot C_{10}H_6\cdot NH_2 \\ | \\ CO\end{matrix}$.

In view of difficulties connected with the preparation of acetyl-1 : 4-naphthylenediamine, diazotised sulphanilic acid was coupled with α-naphthylaminocamphor, and the product reduced. It was then found that the resulting base is even more sensitive than *p*-aminophenylaminocamphor to oxidation by air, and it has therefore heen isolated only in the form of the hydrochloride and the product of condensation with camphorquinone. p-*Sulphobenzeneazonaphthylaminocamphor*, $C_8H_{14}<\begin{matrix}CH\cdot NH\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4\cdot SO_3H \\ | \\ CO\end{matrix}$, separated in the form of a thick, purple paste on adding a solution of the diazonium salt from sulphanilic acid (10·6 grams) to α-naphthylaminocamphor (18 grams) which had been dissolved in glacial acetic acid by adding a small quantity of hydrochloric acid. After two hours, the product changed to dark green crystals, which were filtered and washed with glacial acetic acid followed by acid of increasing dilution with water (Found: C=61·32, 61·67; H=6·30, 6·35; N=7·69. $C_{26}H_{27}O_4N_3S$ requires C=65·41; H=5·66; N=8·80 per cent. $C_{26}H_{27}O_4N_3S,1\frac{1}{2}C_2H_4O_2$ requires C=61·37; H=5·82; N=7·40 per cent.). In another experiment, the initial product remained as a brown sludge, but when kneaded with alcohol it rapidly changed to minute, dark green crystals melting at 213° with decomposition. Rubbed on glass, the green crystals leave a violet stain; they dissolve in sodium carbonate, forming an orange solution which gives purple flocks when acidified.

Reduction to the Base.—The azo-compound (18 grams) was dissolved in a solution containing potassium hydroxide (9 grams) in water (45 c.c.) and alcohol (90 c.c.), gently warmed to prevent

separation of the potassium salt in orange-red crystals, and treated with sodium hyposulphite (5 grams). The temperature rose and the colour diminished, action being completed by further addition of potassium hydroxide (5 grams) and sodium hyposulphite (5 grams), when the pale yellow liquid was diluted largely with water and extracted with benzene. After washing the solvent twice with water, it was shaken vigorously with diluted hydrochloric acid (40 c.c. of 1 : 1), the acid layer being removed and saturated with salt. The major portion of the *hydrochloride* of aminonaphthylaminocamphor, however, separated in the course of several hours from the benzene, being deposited in hard nodules (Found: Cl=10·00. $C_{20}H_{24}ON_2$,HCl requires Cl=10·30 per cent.).

Camphoryl-1-*aminonaphthyl*-4-*iminocamphor* (IX), prepared by heating the hydrochloride of aminonaphthylaminocamphor (5·9 grams) in alcohol with sodium acetate (3 grams) and camphorquinone (2·9 grams), was rapidly deposited as a red powder, separating from hot alcohol in brick-red crystals melting at 195° (Found: N=6·51. $C_{30}H_{36}O_2N_2$ requires N=6·14 per cent.). A solution containing 0·0519 gram in chloroform diluted to 25 c.c. gave α_D 3° 30′ in a 1-dcm. tube, whence $[\alpha]_D$ 1686°; a similar solution in pyridine containing 0·0517 gram gave α_D 4° 12′, whence $[\alpha]_D$ 2031°. These correspond to $[M]_D$ 7688° and 9261°, respectively.

The foregoing experiments were made in the Davy-Faraday Laboratory.

ROYAL INSTITUTION, W. 1.

[*Received, May 18th, 1921.*]

LXXXIX.—*Studies in the Resolution of Racemic Acid[s] by Optically Active Alcohols. Part II. Th[e] Resolution of Atrolactinic and α-Hydroxy-β phenylpropionic Acids by* l-*Menthol.*

By HENRY WREN and EDWARD WRIGHT.

THE experiments which are recorded in the present communicatio[n] arose from the incidental observation that *l*-menthyl *dl*-atrolactina[te] (McKenzie and Wren, T., 1920, **117**, 688) gradually becomes part[ly] crystalline when preserved. Although the persistence of the supe[r]cooled condition is by no means uncommon with initial preparatio[ns] of esters of this type, the fact that the compound in this instance d

not solidify completely even when strongly cooled rendered it not improbable that only one of the diastereoisomerides had separated in the solid state. This was found to be the case, since, when the product was suitably spread on porous paper, *l*-menthyl *d*-atrolactinate was mainly absorbed, leaving a residue of nearly pure *l*-menthyl *l*-atrolactinate. Subsequent experiments showed that the resolution could be effected more readily by crystallisation from light petroleum.

A similar examination of the isomeric *r*-α-hydroxy-β-phenylpropionic acid has shown that a ready resolution may be effected by crystallisation of the *l*-menthyl ester from light petroleum or ethyl alcohol (96 per cent.); the *l*-bornyl ester, on the other hand, is unsuitable for this purpose, since it, like the corresponding compounds of the optically active acids, does not solidify at a convenient temperature.

In several instances, the *l*-menthyl and *l*-bornyl esters of the optically active acids have been prepared from the latter with the object of securing material for seeding and of estimating the solubility; the purpose of these experiments, however, has generally been frustrated by the liquid nature of the compounds.

Experimental.

Resolution of r-*Atrolactinic Acid by* l-*Menthol.*

A. *By Absorption of the Liquid Portion.*—*l*-Menthyl *dl*-atrolactinate (b. p. 190—192°/10—11 mm., $[\alpha]_D$ −67·5° in chloroform solution) was seeded with a small quantity of *l*-menthyl *l*-atrolactinate and preserved at the ordinary temperature and subsequently in an ice-chest for several days until further solidification did not appear to take place. The pasty mass was spread on porous earthenware and afterwards on filter papers, which were frequently renewed. By conducting the latter operation in a powerful press, it was found possible to raise the melting point of the residue to 53·5—54·5°; the product, which weighed 14·2 grams, then had $[\alpha]_D$ −97·5° in chloroform solution, whereas pure *l*-menthyl *l*-atrolactinate melts at 55·5—56° and has $[\alpha]_D$ −102·7° (McKenzie and Wren, *loc. cit.*).

Hydrolysis of the ester with alcoholic potassium hydroxide solution yielded 6·9 grams of acid which melted at 99—110° and had $[\alpha]_D$ −33·8° in ethyl-alcoholic solution. The optical purity of the specimen was not sufficiently high to permit the isolation of the pure *l*-acid by direct crystallisation (compare McKenzie and Clough, T., 1910, 97, 1019), but, by dissolving it in a suitable quantity of benzene and allowing the solution to cool, a less active crop was

removed; the filtrate from this was allowed to evaporate spontaneously and the residue crystallised repeatedly from comparatively large quantities of the same solvent, whereby ultimately a specimen of the *l*-acid was isolated which melted sharply at 115—116° and had $[\alpha]_D^{15}$ −36·1° in ethyl-alcoholic solution (c=2·7252), whereas McKenzie and Clough (*loc. cit.*) give m. p. 116—117°, $[\alpha]_D^{13\cdot 8}$ −37·7° (c=3·354) for the pure acid (Found: C=64·9; H=6·2. Calc., C=65·0; H=6·1 per cent.).

B. *By Crystallisation from Light Petroleum.*—A solution of *l*-menthyl *dl*-atrolactinate (43 grams) in light petroleum (b. p. 40—60°, 50 c.c.) was cooled to −18° and seeded with a small quantity of the pure *l*-ester; the crop which separated was filtered as rapidly as possible through a well-cooled filter, giving thus 8·5 grams of residue which melted at 32—41° and had $[\alpha]_D$ −82·2° in chloroform solution, whilst the substance obtained from the filtrate had $[\alpha]_D$ −61·2°. The crop was purified by repeated cautious crystallisation from light petroleum, whereby finally 1·7 grams of *l*-menthyl *l*-atrolactinate were isolated, which melted at 54—55·5° and had $[\alpha]_D$ −100·9° when dissolved in chloroform. The ester was hydrolysed in the usual manner and gave a specimen of the *l*-acid which melted at 116° and had $[\alpha]_D$ −37·2° in ethyl-alcoholic solution.

In connexion with the experiments just described, *l*-menthyl *d*-atrolactinate was prepared by heating *d*-atrolactinic acid with *l*-menthol during twenty hours at 100° in the presence of a little concentrated sulphuric acid.

l-*Menthyl* d-*atrolactinate* is a colourless, viscous liquid which does not solidify when placed in a freezing mixture of ice and salt or preserved at the laboratory temperature during several months.

It boils at 154—155°/0·03 mm. (Found: C=74·9; H=9·5. $C_{19}H_{28}O_3$ requires C=74·9; H=9·3 per cent.). The following observations of the specific rotation were made:

In chloroform solution:

$$l=2,\ c=1\cdot 8416,\ \alpha_D^{14}\ -1\cdot 55°,\ [\alpha]_D^{14}\ -41\cdot 3°.$$

In ethyl-alcoholic solution:

$$l=2,\ c=1\cdot 5476,\ \alpha_D^{13\cdot 5}\ -1\cdot 82°,\ [\alpha]_D^{13\cdot 5}\ -58\cdot 8°.$$

Resolution of r-α-*Hydroxy*-β-*phenylpropionic Acid by* l-*Menthol.*

A. *By Crystallisation from Light Petroleum.*—*r*-α-Hydroxy-β-phenylpropionic acid (10 grams) was heated with *l*-menthol (23 grams) during sixteen hours at 120°, an intermittent current of dry hydrogen chloride being passed through the mixture. The product

was dissolved in ether and the solution thoroughly agitated with aqueous sodium carbonate solution, which, however, did not remove any hydroxy-acid, thus showing that the esterification had been carried to completion. The crude ester was purified from excess of *l*-menthol in the usual manner and ultimately obtained as a mass of crystalline needles impregnated with oil. The whole product was dissolved in boiling light petroleum and the solution allowed to crystallise; the crop which separated weighed 6 grams, melted at 54—55°, and had $[\alpha]_D$ −39·6° when dissolved in chloroform. After several further crystallisations from the same solvent, *l*-menthyl *d*-α-hydroxy-β-phenylpropionate was isolated in the pure condition; it melted at 63—63·5° and had $[\alpha]_D^{15}$ −37·5° in chloroform, whereas McKenzie and Wren (*loc. cit.*) give m. p. 63—63·5°, $[\alpha]_D^{16.5}$ −36·9° for the synthetic ester (Found: C=74·6; H=9·6. Calc., C=74·9; H=9·3 per cent.).

For the isolation of the *d*-acid, the final crop of the *l*-menthyl *d*-ester was united with the residues obtained by the evaporation of the mother-liquors from all the crystallisations with the exception of the first, and hydrolysed with a slight excess of aqueous alcoholic potassium hydroxide solution. The crude acid was isolated from the solution in the usual manner and purified by crystallisation from water. The final crop melted at 123° and had $[\alpha]_D^{15}$ +18·2° in ethyl-alcoholic solution; these data are in harmony with those (m. p. 124—125°, $[\alpha]_D^{18}$ +18·5°) recorded by McKenzie and Wren (T., 1910, **97**, 1357) for the *d*-acid prepared by resolving the *r*-acid with morphine.

The residue obtained by the evaporation of the filtrate from the initial crystallisation was hydrolysed similarly and yielded a mixture of *r*- and *l*-α-hydroxy-β-phenylpropionic acids which had $[\alpha]_D$ −7·0° in ethyl-alcoholic solution. Successive crystallisations of this material from benzene and water gave the pure *l*-acid, which melted at 123—124° and had $[\alpha]_D^{17}$ −18·7° in ethyl alcohol.

B. *By Crystallisation from Alcohol* (96 per cent.).—The *l*-menthyl ester obtained from 17 grams of the *r*-acid by the method described above was crystallised from ethyl alcohol (96 per cent.) and the crop and residue obtained by evaporation of the filtrate were hydrolysed separately to the corresponding acids.

That obtained from the former melted at 97—110° and had $[\alpha]_D$ +13·7°; by successive crystallisations from water and benzene, it readily yielded the pure *d*-acid, m. p. 123—124°, $[\alpha]_D^{18}$ + 18·4° in ethyl-alcoholic solution. In a similar manner the latter gave the pure *l*-acid, which melted at 123° and had $[\alpha]_D^{17}$ −18·7° when dissolved in ethyl alcohol.

The following esters were prepared from the requisite alcohols and

acids by the hydrogen chloride method, heating being effected at 120° for about twelve hours.

l-*Menthyl* l-*α-hydroxy-β-phenylpropionate* is a pale yellow, viscous liquid which does not solidify when placed in a freezing mixture of ice and salt or when preserved at the ordinary temperature. It boils at 212—214°/12 mm. (Found: C=74·4; H=9·4. $C_{19}H_{28}O_3$ requires C=74·9; H=9·3 per cent.). Its specific rotation was observed in solution in chloroform and alcohol:

In chloroform solution:

$l=2$, $c=2·254$, α_D^{17} −3·63°, $[\alpha]_D^{17}$ −80·5°.

In ethyl-alcoholic solution:

$l=2$, $c=2·1624$, α_D^{16} −2·05°, $[\alpha]_D^{16}$ −47·4°.

On complete hydrolysis of the ester with aqueous ethyl-alcoholic potassium hydroxide solution, an acid was obtained which, without further purification, melted at 122—123° and had $[\alpha]_D$ −17·8° in ethyl alcohol, showing thus that the high temperature of the distillation had not induced racemisation and that the ester is as optically stable towards alkali as its diastereoisomeride (compare McKenzie and Wren, T., 1920, **117**, 690).

l-*Bornyl* d-*α-hydroxy-β-phenylpropionate* is a pale yellow, viscous liquid which could not be caused to solidify. It boils at 209°/11 mm. (Found: C=75·7; H=8·7. $C_{19}H_{26}O_3$ requires C=75·5; H=8·7 per cent.). Determinations of the specific rotation were made in chloroform and ethyl alcohol.

In ethyl-alcoholic solution:

$l=2$, $c=2·6304$, α_D^{17} −1·93°, $[\alpha]_D^{17}$ −36·7°.

In chloroform solution:

$l=2$, $c=2·586$, α_D^{15} −0·25°, $[\alpha]_D^{15}$ −4·8°.

The ester is not racemised appreciably at the high temperature required by distillation or by aqueous alcoholic potassium hydroxide solution, since the acid obtained by its hydrolysis melted at 121—122° and had $[\alpha]_D$ + 18·0° in ethyl-alcoholic solution.

l-*Bornyl* l-*α-hydroxy-β-phenylpropionate* is a pale yellow, viscous oil which boils at 203·5°/9 mm. (Found: C=75·4; H=8·7. $C_{19}H_{26}O_3$ requires C=75·5; H=8·7 per cent.). The following determinations of the specific rotation were made.

In ethyl-alcoholic solution:

$l=2$, $c=2·4884$, α_D^{17} −0·82°, $[\alpha]_D^{17}$ −16·5°.

In chloroform solution:

$l=2$, $c=2·4812$, α_D^{17} −2·48°, $[\alpha]_D^{17}$ −49·9°.

It is remarkable that whereas the *l*-ester exhibits a higher specific

rotation in chloroform than in ethyl alcohol, the reverse is the case with the diastereoisomeride.

When hydrolysed with aqueous ethyl-alcoholic potassium hydroxide solution, the *l*-ester yielded *l*-α-hydroxy-β-phenylpropionic acid, which, without being further purified, melted at 122—123° and had $[\alpha]_D$ −17·9° in ethyl-alcoholic solution.

l-Bornyl r-*α-hydroxy-β-phenylpropionate* is an almost colourless, viscous liquid which boils at 213—214°/14 mm. (Found: C=75·7; H=8·5. $C_{19}H_{26}O_3$ requires C=75·5; H=8·7 per cent.). The specific rotation was observed in ethyl-alcoholic solution:

$$l=2,\ c=4{\cdot}0192,\ \alpha_D^{12}\ -2{\cdot}10^\circ,\ [\alpha]_D^{12}\ -26{\cdot}1^\circ.$$

The mean value of the specific rotations of the esters of the optically active acids is —26·6° under closely similar conditions.

When hydrolysed, the ester gave *r*-α-hydroxy-β-phenylpropionic acid, which was optically quite inactive.

Attempts were also made to resolve *r*-β-hydroxy-β-phenylpropionic acid by means of *l*-menthol. The acid, however, appeared to be somewhat readily changed in the presence of mineral acid, and the esters which were obtained were invariably contaminated with *l*-menthyl cinnamate.

One of us desires to express his indebtedness to Mr. Robert MacIntyre for able assistance in the early portions of the work and to the Research Fund Committee of the Royal Society for a grant which has defrayed part of the cost of the investigation.

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BELFAST. [*Received, May 3rd*, 1921.]

XC.—*The Hydrolysis of Cotton Cellulose.*

By GORDON WICKHAM MONIER-WILLIAMS.

THE investigations hitherto carried out on the hydrolysis of cellulose have been critically reviewed by Irvine and Soutar (T., 1920, **117**, 1489). They point out that up to the date of their work, crystalline glucose had never been obtained in even approximately quantitative yield from the products of hydrolysis, and that conclusions drawn as to the amount of glucose present had invariably been based on the rotation and copper reduction of an uncrystallisable syrup. Irvine and Soutar found that if cellulose was treated with acetic anhydride and sulphuric acid, the mixture of polysaccharide acetates

obtained could be converted by heating with methyl alcohol and hydrochloric acid into a crystalline methyl-glucoside, which gave pure crystalline glucose on hydrolysis. The yield of glucose obtained was 85 per cent. of the theoretical quantity.

The results recorded below are the outcome of an attempt to repeat Ost and Wilkening's work on the direct hydrolysis of cellulose by 72 per cent. sulphuric acid (*Chem. Zeit.*, 1910, **34**, 461). Preliminary experiments, following exactly the method used by these investigators, invariably gave a syrup from which no crystalline glucose could be prepared. Eventually the following procedure was adopted :

Ten grams of cotton-wool were dissolved in 50 c.c. of 72 per cent. sulphuric acid, and the dark-coloured, viscous solution was allowed to remain for one week at room temperature. The cotton-wool used contained 6·93 per cent. of moisture, estimated by drying to constant weight in a water-oven at 94°, and 0·13 per cent. of ash. The sulphuric acid solution was diluted to five litres with water, and boiled under reflux for a total time of fifteen hours. Traces of volatile fatty acids distilled into the condenser. A slight quantity of a dark-coloured, flocculent precipitate was present in the liquid. This was filtered off, dried, and weighed (0·1620 gram). The liquid after filtering was almost colourless. It was neutralised to litmus paper with barium carbonate, filtered clear from the precipitate of barium sulphate, and evaporated to dryness under reduced pressure (40 mm.). It was found in a preliminary experiment that alkalinity developed during the concentration. This appeared to be due partly to traces of sodium carbonate in the barium carbonate used. A few drops of methyl-red were therefore added to the distilling flask, and the liquid during concentration was kept neutral to this indicator by repeated addition of $N/10$-sulphuric acid. The residue from the distillation was extracted under reflux with methyl alcohol, free from acetone. After being filtered from insoluble barium and sodium sulphates, and decolorised by boiling with a small quantity of animal charcoal, the methyl-alcoholic solution was evaporated in a current of dry air at a low temperature. Crystals soon formed on the sides of the vessel, and the residue after evaporation of the methyl alcohol was completely crystalline and almost white. It weighed 9·718 grams, and on analysis gave the following figures :

		Mean.
Moisture (by drying in water-oven)	3·36	3·28 per cent.
Moisture (by *sp. gr.* of 10 *per cent. solution*)	3·20	
Ash		1·53 ,, ,,
Glucose (by polarimeter)	94·73	94·57 ,, ,,
Glucose (by copper reduction)	94·41	
		99·38 ,, ,,

On recrystallisation from absolute alcohol, the residue gave a large crop of white crystals, m. p. 144—145° (uncorr.), and a glucose-phenylosazone, m. p. 204—205° (uncorr.). Allowing for the moisture and ash in the original cellulose, and for the small quantity (0·162 gram) of material which was not dissolved by the acid, the yield of crystalline glucose, calculated from the analysis of the crude product, amounted to 90·67 per cent. of the theoretical quantity. No other product of hydrolysis could be detected either in the barium sulphate precipitate or in the distillate from the evaporation. It is possible that slight losses of sugar may be due to incomplete washing of the voluminous barium sulphate precipitate. Small amounts may also be carried over mechanically during the distillation of the liquid under reduced pressure, or removed by the treatment with animal charcoal. These points are being further investigated.

MINISTRY OF HEALTH,
WHITEHALL, S.W. [*Received, April 22nd*, 1921.]

XCI.—*Amylases of the Cereal Grains—Rye.*

By JULIAN LEVETT BAKER and HENRY FRANCIS EVERARD HULTON.

IN a paper published by one of us (T., 1902, **77**, 1177) an account was given of the properties of the amylase of barley. This enzyme, which has only a slight liquefying action on starch paste, when allowed to act on soluble starch produced about 40 per cent. of α-amylodextrin and 60 per cent. of crystallisable maltose. These were the sole products formed in the first stage of the conversion; if, however, the action be allowed to continue for many hours, a small amount of dextrose will be formed.

In the course of an examination of the amylolytic capacity of raw materials containing starch used in distilleries, Windisch and Jetter (*Zeitsch. Spiritusind.*, 1907, **30**, 541) recorded that ungerminated rye (*Secale cereale*) contains sufficient amylase to saccharify practically all the starch present in the grain. These authors also state that in some Continental distilleries alcohol is made from rye alone without the use of barley malt.

It seems somewhat remarkable that the amylase of rye should stand out in contrast to other cereals in thus appearing to possess the properties of an amylase of germinated grain, as it might be

anticipated that the amylases of the ungerminated *Gramineæ* would be more or less similar. We thought, therefore, it would be of interest to study the enzymes of rye and to see in what respect they differ from those of barley.

EXPERIMENTAL.

When a filtered aqueous extract of rye is added to a 4 per cent. starch paste, liquefaction rapidly takes place and after a few hours the constants of the conversion products will be $[\alpha]_D + 145—155°$ and R 65—70. The iodine reaction varies from brown to light blue. When the conversion is fractionated by means of alcohol, the soluble portion consists of almost pure crystalline maltose and the insoluble portion of a dextrin closely resembling α-amylodextrin (*loc. cit.*). Several conversions have been carried out, of which the following may be regarded as typical. Two litres of a 3 per cent. potato-starch paste were hydrolysed at 50° with the amylase separated by alcoholic precipitation from 50 grams of an aqueous extract of rye. Portions were removed at intervals, immediately pipetted into a sufficient volume of boiling water to stop further enzymic action, and analysed. The following results were obtained:

Action of Ungerminated Rye Diastase on Starch Paste at 50°.

Time hr.	Time mins.	$R_{3\cdot93}$ (Reducing power as maltose.)	$[\alpha]_{D3\cdot93}$	Time hrs.	Time mins.	$R_{3\cdot93}$ (Reducing power as maltose.)	$[\alpha]_{D3\cdot93}$
0	2	16·1	—	0	40	56·6	+155·6°
0	5	23·6	—	1	0	60·1	+156·3
0	10	33·4	—	2	0	64·7	+155·1
0	15	39·7	—	3	0	65·2	+156·1
0	20	47·7	—	20	0	72·4	+147·8
0	30	53·4	—				

The course of the hydrolysis, when expressed graphically, differs slightly from that of a barley amylase conversion (*loc. cit.*), the rye curve being more regular. At the end of three hours the constants, whether barley or rye amylase be the hydrolyst, are identical.

To separate the products formed by the action of rye amylase on starch for the purpose of a close examination, the enzyme from 100 grams of rye was isolated and allowed to act on 3 litres of 3 per cent. starch paste at 50° for three hours. After raising to the boiling point and filtering, the conversion had a purplish-brown iodine reaction, a specific rotatory power of $[\alpha]_{D3\cdot93} + 150°$, and a reducing power $R_{3\cdot93} = 65·2$ per cent. of maltose. The conversion was evaporated to a volume of 500 c.c. and poured into 3·5 litres of 94

per cent. alcohol, the precipitated dextrin was dissolved in water, and again precipitated with alcohol. By this procedure about 22 per cent. (on the weight of the starch taken) of a dextrin was obtained having the constants $R_{3\cdot93}$ 1·5 and $[\alpha]_{D3\cdot93}$ 184·1°. The matter in the alcoholic solutions was evaporated to a syrup and maltose separated on standing a few hours in a state of purity. Fractionation by means of alcohol of a number of similar conversions gave the same order of results; it may therefore be concluded that when the amylase of rye acts on starch paste only two products are formed, namely, a dextrin of an R of 1 to 2 per cent. and crystalline maltose.

The dextrin, with constants R 1·5 and $[\alpha]_D$ 184·1°, resulting from the action of rye amylase on starch, was submitted to the further hydrolytic action for twelve hours at 50° with (1) the amylase of rye and (2) the amylase of malted barley:

Rye amylase	$[\alpha]_{D3\cdot93}$	174·9°
	$R_{3\cdot93}$	14·7
Iodine reaction		Deep brown.
Malt amylase	$[\alpha]_{D3\cdot93}$	154·9°
	$R_{3\cdot93}$	55·5
Iodine reaction		nil.

From these results it would appear that the products of the action of the amylases of ungerminated rye and germinated barley on this dextrin are of a similar character to those obtained when α-amylodextrin is acted on by ungerminated and germinated barley amylase (*loc. cit.*).

Since continued fractionation with alcohol failed to alter the specific rotatory power or reducing power of the dextrin with the constants $[\alpha]_D$ 184·1° and R 1·5, we consider we are justified in concluding that it is identical with the α-amylodextrin previously described (*loc. cit.*).

Action of the Amylase of Malted Rye on Starch.

Having shown that rye, as compared with barley, although yielding similar products, possesses a greater enzymic (liquefying) activity towards starch paste, we considered it would be of interest to investigate the action of the amylase of germinated rye on starch.

Some rye was malted in the laboratory and dried at 40°. The diastatic power expressed on the Lintner scale was 100°. A cold aqueous extract of the malted rye or the amylase separated by alcoholic precipitation was allowed to act on a 3 per cent. starch paste at 50°, in the proportion of the enzyme from 1 gram of malted rye to 1 gram of starch. Liquefaction of the starch paste took place

rapidly and the iodine reaction disappeared in about fifteen minutes. The specific rotatory power of the conversion products varied from 146—149° and the reducing power from 80—84 per cent. of maltose. Several conversions were made with similar results. It will be noted the constants resemble those resulting from the action of malt amylase on starch paste. When fractionated in the customary manner with alcohol, crystalline maltose was obtained with greater ease than in the case of a malt amylase starch conversion. The insoluble portion (dextrin) when analysed had a specific rotatory power of 171·8° and a reducing power of R 31·4; by continued fractionations with alcohol a dextrin was finally obtained with the constants $[\alpha]_D$ 180·1° and R 12·6. This dextrin was isolated, and extracted with boiling 85 per cent. alcohol for several hours. After this treatment the constants were $[\alpha]_D$ 181·9° and R 11·4, and when dried over sulphuric acid the dextrin was not hygroscopic; it would appear, therefore, that the limit of the capacity for this dextrin to be fractionated by alcohol has been reached. On further treatment of this dextrin with malt amylase for three hours at 50° there was evidence of a slight hydrolysis, the reducing power being raised only a few points.

This final dextrin was unfermentable, and, although possessing a reducing power, contained no free maltose. That this is the case is confirmed by the following experimental data. Some pure maltose was added to the dextrin in the proportions: maltose 37·7 per cent., dextrin 62·3 per cent. A portion of this mixture was fermented, control fermentations being carried out on the pure maltose and on the dextrin. Another portion of the mixed maltose and dextrin was poured into alcohol.

Fermentation.—The loss was 35 per cent., corresponding to the whole of the added maltose but no more. The constants of the unfermented residue were $[\alpha]_D$ 180·6° and R 14, figures which agree well with the original dextrin.

Treatment with Alcohol.—The mixture of maltose and dextrin was poured into alcohol and the dextrin precipitated had the constants $[\alpha]_D$ 181·7° and R 12·8. It is thus apparent that the alcohol has dissolved the whole of the added maltose and that the dextrin remained unaltered.

It may be concluded that the apparent maltose in this dextrin is in a state of combination and not merely in association. It is therefore an unfermentable, reducing dextrin, incapable of fractionation by alcohol.

Up to this point two products resulting from the action of malted rye amylase on starch have been isolated, namely, maltose and the dextrin just described. It now became necessary to ascertain i

other dextrins are to be found in the conversion products, since it is well known that a number of ill-defined dextrins of varying molecular weights can be isolated from the products of a malted barley amylase starch conversion.

A specimen of the dextrin above referred to ($[\alpha]_D$ 171·8°; R 31·8) was submitted to the action of malt amylase for two and a half hours at 50°. The constants were then found to be $[\alpha]_D$ 173° and R 30·6, this result showing that no effect was produced and that the dextrin was not associated with degradable maltodextrin, notwithstanding its high apparent maltose content. Confirmatory evidence that the conversion products resulting from the action of malted rye amylase on starch consist solely of crystallisable maltose and a dextrin, is afforded by submitting such products to fermentation by *S. cerevisiæ.* We found that in three days a conversion having the constants $[\alpha]_D$ 149·5° and R 77 lost 70·6 per cent. of the solids in solution and that the calculated constants of the matter fermented closely approached those of maltose. The unfermented portion contained a trace of maltose and the impurities from the yeast. The constants, however, were not far removed from those of the dextrin ($[\alpha]_{D3 \cdot 93}$ 181·9°; R 11·4) described above.

Conclusions.

(1) Ungerminated rye amylase, when allowed to act on potato-starch paste at 50°, readily liquefies the paste and yields α-amylodextrin (R 1·5; $[\alpha]_D$ 184·1°) and maltose, which can be obtained crystalline after one fractionation with alcohol. This is in accordance with the behaviour of ungerminated barley diastase.

(2) The amylase of germinated rye under the same conditions yields a non-hygroscopic, unfermentable reducing dextrin (R 10·8; $[\alpha]_D$ 181·9°) and crystalline maltose. That there is no production of the intermediate, degradable maltodextrins such as are formed by the action of malt amylase on starch is shown by the fact that almost the whole of the apparent maltose in the original conversion is fermentable by yeast and that the intermediate alcoholic fractions are undegradable by malt amylase.

THE STAG BREWERY,
PIMLICO, S.W.

[*Received, April 23rd, 1921.*]

XCII.—*The Formation and Stability of* spiro-*Compounds. Part IV. Ketones Derived from Open-chain and Cyclic Glutaric Acids.*

By George Armand Robert Kon.

The tetrahedral theory of the structure of the carbon atom which forms the basis of the Baeyer strain hypothesis leads, as is well known, to the prediction that five-membered carbon rings are those which should be most easy of formation, whereas rings composed of a greater or a smaller number of carbon atoms are correspondingly more difficult to produce, the figures calculated by Baeyer (*Ber.*, 1885, **18**, 2278; 1890, **23**, 1275) for the angles through which the normal tetrahedral angle (109° 28′) has to be deflected in order to form the ring—a figure which Baeyer regards as indicating the relative stabilities of the rings when once formed—being

*cyclo*Propane	24° 44′	*cyclo*Hexane	−5° 16′
*cyclo*Butane	9° 44′	*cyclo*Heptane	−9° 33′
*cyclo*Pentane	0° 44′	*cyclo*Octane	−12° 51′

Although experimental evidence is on the whole in support of this hypothesis, there are certain outstanding discrepancies in view of which it appears necessary to remould the theory in a somewhat fundamental manner. For this purpose careful comparative investigations of the conditions governing the formation of the different carbon rings are essential, and it is the purpose of the present paper to deal with the factors affecting the closing and disruption of four-membered carbon rings, in particular of rings which may be described as extra-annular, that is to say, those which are external to some other ring.

Now, of the many methods which have been used for the preparation of alicyclic derivatives two are of primary importance They are:

(1) The distillation of the calcium salts of dibasic acids (Wislicenus *Annalen*, 1893, **275**, 309).

(2) The elimination of alcohol from esters of dibasic acids (Dieckmann, *Ber.*, 1894, **27**, 102).

These two methods are of particular interest for purposes of comparison because they are both concerned with the transformation of dibasic acids into ring ketones. Together they constitute some of the strongest evidence supporting the Baeyer strain hypothesis for, hitherto, the only members of the series of dibasic acids whic

have been found to undergo these reactions at all smoothly are those of the adipic and pimelic series, that is, those which produce five- and six-membered ring ketones respectively. Moreover, it is *of importance to note that those acids which can be converted* into ketones are incapable of yielding anhydrides under the usual experimental conditions, and that those acids which can be converted into anhydrides have not been found to produce ring ketones by means of either of the reactions mentioned above. Thus, whilst succinic and glutaric acids readily yield anhydrides but not corresponding cyclic ketones, adipic, pimelic, and suberic acids give no stable anhydrides, but, on the other hand, are readily converted into ketones.*

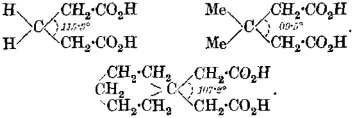
In each case the limiting condition appears to lie between those which hold in glutaric and in adipic acids. There can, however, be *no question but that there is a very great difference of stability* between the cyclic products derived from these two acids, and that in order to ascertain the limiting condition with any degree of accuracy the investigation of compounds having intermediate stabilities is required.

In a recent paper (this vol., p. 305) Ingold has directed attention to the remarkable effect of the *gem*-dialkyl group in promoting the formation of three-, four-, and five-membered carbon rings, as well as of certain five- and six-membered heterocyclic rings. This is ascribed to the fact that in a normal polymethylene chain the angle between each pair of carbon-to-carbon valencies is not 109·5°, as the Baeyer hypothesis requires, but *a greater angle, namely, 115·3°*, which is governed by the principle that the spatial arrangement of valencies not concerned in ring formation is determined by the relative atomic volumes of the atoms to which they are attached. This hypothesis receives further support from the relative ease of formation and the stabilities of the various types of carbon ring, in particular from the difficulty with which the closure of the *cyclo*-butane ring is attended (*loc. cit.*) and from the almost equal stabilities of five- and six-membered carbon rings. When, however, a *gem*-dialkyl group is introduced into a normal polymethylene chain, the angle between the carbon valencies is deformed from 115·3° to 109·5°; *consequently, the formation of the carbon rings the internal*

* It is true that in a preliminary note (*J. Russ. Phys. Chem. Soc.*, 1897, **29**, 280) Zelinsky states that two of his pupils, Yakovleff and Bieltzoff, had succeeded in preparing small quantities of dimethyl- and diethyl-*cyclo*butanones by distilling the barium salts of the corresponding dialkylglutaric acids. These ketones, however, were only characterised by somewhat indefinite boiling points, and no proofs were given of their cyclic structure. *It is shown* in this paper (p. 815) that there is reason to doubt the correctness of the constitutions assigned to them.

angles of which are less than 115·3°, namely, the *cyclo*propane, *cyclo*butane, and *cyclo*pentane rings, takes place with greater readiness from the *gem*-substituted than from the unsubstituted open-chain.

When the constituents of the *gem*-grouping themselves form part of a ring, a further convergence may occur. Thus it has been shown by Beesley, Ingold, and Thorpe (T., 1915, **107**, 1080; see also Ingold and Thorpe, T., 1919, **115**, 320) that if the angle between the valencies joining the acetic acid residues to the central carbon atom of ββ-dimethylglutaric acid is 109·5°, the corresponding angle in *cyclo*hexanediacetic acid is appreciably less, namely, 107·2°. Consequently the formation of rings by the interaction of the acetic residues, or substituents attached thereto, takes place with greater facility in the latter case than in the former:



These *gem*-substituted glutaric acids, therefore, occupy various positions intermediate between glutaric and adipic acids in the scale of stability of the ketones to which they should give rise; in particular, they, in all probability, occupy positions in the restricted region common to ketone- and anhydride-forming dibasic acids. If "figure of instability" * be used to represent the various degrees of instability of the different potential ring compounds, then there must be some "critical figure" corresponding to the limit beyond which the closure of the ring by a given method becomes impossible. Since the figures for the ketones derived from the various open-chain and cyclic *gem*-substituted glutaric acids clearly lie in the region of the critical figure, it should be possible by an examination of these cases to make a close estimate of this important constant. It was therefore decided in the first

* The author is asked by Prof. J. F. Thorpe to give the following definition of the term "figure of instability." In the first place, it must be clearly understood that it is not suggested that the alteration in the tetrahedral angle produces any distortion of the molecule such as would lead to a form of stereoisomerism which has not yet been observed and which it is unnecessary for the present purposes to consider capable of occurrence. The stress set up by the altered tetrahedral angle is borne by the whole molecule, partly by the curved valencies and partly by the carbon atoms themselves. It does not lead to the production of asymmetry, but gives rise to a condition of strain of which the "figure of instability" is a direct measure.

place to investigate, besides glutaric, β-methylglutaric, and ββ-dimethylglutaric acids, the three cyclic derivatives which have already been prepared, namely, *cyclo*pentanediacetic, *cyclo*hexanediacetic, and *cyclo*heptanediacetic acids, with reference to their capacity for passing into ring ketones by means of the reactions mentioned on p. 810. The present part of this series deals primarily with the complete investigation of the products formed when the calcium salts of these acids are distilled.

Now it is shown in this paper that, although the cyclic ketones derived from the different glutaric acids in no case survive the conditions of a calcium–salt distillation, it is possible, fortunately, to recognise their formation with certainty owing to the fairly simple character of the decompositions which ensue. It is therefore of the highest importance to observe that, whilst with glutaric acid and β-methylglutaric acid there was obtained no evidence of the production of four-carbon, cyclic ketones, in every case in which a *gem*-substituted glutaric acid was used, namely, ββ-dimethylglutaric acid, ββ-diethylglutaric acid, and *cyclo*pentane-, *cyclo*hexane-, and *cyclo*heptane-diacetic acids, the formation of the ring ketone was the primary reaction.

Comparatively few investigations on the thermal decomposition of compounds containing alicyclic rings of the more highly strained types appear to have been carried out hitherto, but those which have been made have shown unquestionably that the primary reaction is always a transformation into the corresponding unsaturated isomeride. Thus Tanatar showed that *cyclo*propane passes at red heat into propylene (*Ber.*, 1896, **29**, 1297; 1899, **32**, 702), whilst Ipatieff and Hahn (*Ber.*, 1903, **36**, 2014, 2016) proved that in the presence of a contact material such as alumina the reaction takes place below 400°, and that methyl*cyclo*propane and 1 : 1-dimethyl*cyclo*propane undergo an analogous transformation when subjected to similar conditions.

$$H_2C{<}\begin{matrix}CH_2\\ |\\ CH_2\end{matrix} \quad\longrightarrow\quad CH_2{:}CH{\cdot}CH_3$$

$$MeHC{<}\begin{matrix}CH_2\\ |\\ CH_2\end{matrix} \quad\longrightarrow\quad CHMe{:}CH{\cdot}CH_3$$

$$\begin{matrix}Me\\ Me\end{matrix}{>}C{<}\begin{matrix}CH_2\\ |\\ CH_2\end{matrix} \quad\longrightarrow\quad CMe_2{:}CH{\cdot}CH_3$$

Consequently it is not altogether surprising that the cyclic ketones produced during the calcium–salt distillation, in all those cases in which they are undoubtedly the *primary* products, isomerise under the experimental conditions employed, yielding unsaturated ketones in agreement with Tanatar and Ipatieff's observations.

Thus the cyclic ketone from dimethylglutaric acid yields mesityl oxide (I),

$$\begin{matrix}Me\\Me\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\\CH_2\end{matrix}\!>\!CO \longrightarrow \begin{matrix}Me\\Me\end{matrix}\!>\!C{:}CH{\cdot}COMe \quad (I.)$$

$$H_2C\!<\!\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\\CH_2\end{matrix}\!>\!CO \longrightarrow H_2C\!<\!\begin{matrix}CH_2{\cdot}CH_2\\CH_2{-}CH\end{matrix}\!\geqslant\!C{\cdot}CH_2{\cdot}COMe \quad (II.)$$

whilst that from *cyclo*hexanediacetic acid is transformed into Wallach's *cyclo*hexenylacetone (II).* Similarly, *cyclo*pentanediacetic acid yields *cyclo*pentenylacetone (III), *cyclo*heptanediacetic acid *cyclo*heptenylacetone (IV), and ββ-diethylglutaric acid the ketone (V).

$$\begin{matrix}CH_2{\cdot}CH_2\\CH_2{-}CH\end{matrix}\!\geqslant\!C{\cdot}CH_2{\cdot}COMe \quad (III.) \qquad \begin{matrix}CH_2{\cdot}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2{-}CH\end{matrix}\!\geqslant\!C{\cdot}CH_2{\cdot}COMe \quad (IV.)$$

$$\begin{matrix}Et\\CHMe\end{matrix}\!\geqslant\!C{\cdot}CH_2{\cdot}COMe \quad (V.)$$

No trace, however, of the corresponding unsaturated ketones could be isolated from the distillates of the calcium salts of glutaric and β-methylglutaric acids. In each of these cases the yield of distillate was very small and its character quite different from that of the distillates from the ββ-disubstituted glutarates already mentioned. In fact, it was an exceedingly difficult matter to identify any of the products with certainty, and almost impossible to account for any considerable proportion of the mixture as pure separated substances. However, the experiments carried out (see pp. 828—830) with the calcium salts of these two acids make it evident that the decompositions which take place on distillation are of a deep-seated character, and, unlike the other cases dealt with, cannot be traced to the formation of cyclic ketones.

With regard to the unsaturated ketones obtained from the ββ-disubstituted glutaric acids, it should be added that an exhaustive investigation of the distillates revealed in each case the presence

* This ketone and a few of its homologues have been prepared by Wallac (*Annalen*, 1912, **394**, 376), who assigned to them the above constitutic mainly on account of their optical properties. A similar constitution temporarily assigned to the new ketones (III), (IV), and (V), as their properti are undoubtedly similar.

The intracyclic character of the double bond in all these compounds i however, called in question by some experiments now in progress in th laboratory, and it is possible that the alternative formulæ of the ty $\begin{matrix}{\cdot}CH_2\\{\cdot}CH_2\end{matrix}\!>\!C{:}CH{\cdot}COMe$ may have to be substituted for those given above.

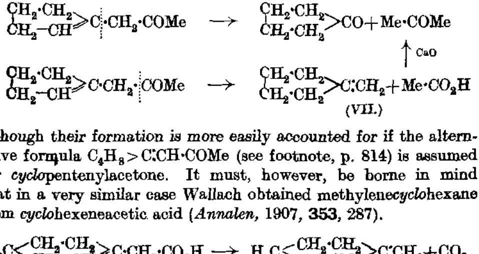
of three decomposition products evidently derived from the unsaturated substances by the hydrolytic action of the water which was invariably present under the conditions of the distillation. Thus from dimethylglutaric acid there were obtained acetone and β-methylpropylene :

$$CMe_2 \vdots CH{\cdot}COMe \longrightarrow CMe_2O + Me{\cdot}CO{\cdot}Me$$
$$\uparrow CaO$$
$$CMe_2{=}CH | {\cdot}COMe \longrightarrow CMe_2{=}CH_2 + Me{\cdot}CO_2H$$

whilst *iso*phorone (VI), which was also isolated in this case, was probably formed by the condensation, under the influence of the calcium oxide, of one molecule of mesityl oxide with one of acetone :

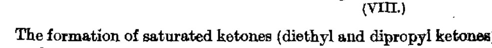
(VI.)

Similar products were found in the other cases, but the character of the least volatile constituents could not be elucidated with certainty. Acetone and a hydrocarbon of the general formula $CR_2{:}CH_2$ were isolated in each case, and also, in the cases of *cyclo*pentanediacetic and ββ-diethylglutaric acids, *cyclo*pentanone, and diethyl ketone respectively. The nature of these products clearly accords with the general scheme,



(VII.)

although their formation is more easily accounted for if the alternative formula $C_4H_8{>}C{:}CH{\cdot}COMe$ (see footnote, p. 814) is assumed for *cyclo*pentenylacetone. It must, however, be borne in mind that in a very similar case Wallach obtained methylene*cyclo*hexane from *cyclo*hexeneacetic acid (*Annalen*, 1907, **353**, 287).



(VIII.)

The formation of saturated ketones (diethyl and dipropyl ketones) was also observed by Yakovleff and Bieltzoff (*loc. cit.*) in the cases studied by them. These substances would be expected to result from the fission in accordance with the above scheme of compounds of the general type $CH_2{:}CR{\cdot}CO{\cdot}CH_2R$ (where R=Me or Et) and it

appears highly probable from the results of the present investigatio that the Russian observers were actually dealing with compound of this type.

[The following note has been written by Mr. C. K. Ingold.]

Probably the best analytical expression with which to identif the figure of instability for any type of ring is that for the maxima curvature of its valencies (Ingold and Thorpe, *loc. cit.*) in the limitin condition in which they are the seat of the whole of the intra molecular strain. This curvature may be defined as $\frac{\delta\alpha}{\delta s}$, where *is the inclination of the straight path to any tangent to the corre sponding curved path, and ds is an element of the latter. If 2 be the inclination between two adjacent terminal tangents at point of junction of two curved paths, then for any given type o* ring θ will differ from $\alpha - \int ds\frac{\delta\alpha}{\delta s}$ only by a quantity which, so far a the partial differentiation is concerned, is a constant. Hence, fo an n-membered ring, the figure of instability reduces to

$$\left[\frac{\delta\alpha}{\delta s}\right]_{s=0} = -2\cos\left(\theta+\frac{\pi}{n}\right),$$

since the variability of the differential is negligible (*loc. cit.*). Fo four-membered rings the expression becomes

$$\sqrt{2}\,(\sin\theta - \cos\theta).$$

The application of these formulæ to the cases under discussion clearly involves the tacit assumption that it is unnecessary to make any special allowance for the influence of the ketonic group on the strains borne by the cyclic valencies. That this view is not altogether justified has already been indicated in general terms (Ingold, *loc. cit.*), but, unfortunately, it is not possible at the present time to make any precise estimate of the effect on stability of the cyclic ketonic group. It happens, however, that this is not a matter of prime importance in the present connexion, for, as the ketone groups are similar both in number and situation in all the cases here dealt with, the scale of relative values of the figures of instability as calculated by the method given will still remain valid, although the reduction of these figures to any absolute standard may require the introduction of a correction into all of them.

It is necessary, therefore, merely to substitute appropriate values for θ in the above expressions in order to obtain figures of instability for the various cyclic ketones. A method of calculating θ for those ketones containing no second ring attached to the first has already

been described in the paper referred to above (Ingold, *loc. cit.*), whilst the general expression

$$\cos \theta = \tfrac{1}{4}\{\sqrt{\cos^2 \beta + 8} - \cos \beta\}$$

for the same angle for ketones which correspond with the various cyclic *gem*-diacetic acids, and which are therefore *spiro*-compounds, has been given in Part III of this series (Becker and Thorpe, T., 1920, **117**, 1579).

The arithmetical figures to which these formulæ lead for the instabilities of the ketones corresponding with the normal-chain dibasic acids are as follows:

Succinic acid	0·927	Pimelic acid	0·084*
Glutaric ,,	0·436	Suberic ,,	0·203*
Adipic ,,	0·126*	Azelaic † ,,	0·343

It will be noticed that only those acids indicated by the asterisk have actually been shown to yield the appropriate ketones when their calcium salts are distilled. The figure 0·436, therefore, clearly represents a ketone too unstable to survive the conditions of a calcium-salt distillation, even if originally formed; on the other hand, a ketone of instability 0·126 is sufficiently stable to be prepared in this way. The critical figure, therefore, lies somewhere in the rather wide interval between 0·436 and 0·126. Whether this can be narrowed down to the interval between the figures 0·343 and 0·203 for azelaic and suberic acids is doubtful, as in these cases the figures given by the formulæ are actually negative and the significance, if any, of the sign (omitted in the table) is uncertain.

The manner in which the interval between 0·436 and 0·126 is subdivided by the figures representing the substituted glutaric acids is exhibited in the following table:

[Glutaric acid	0·436]	*cyclo*Hexanediacetic acid	0·301
*cyclo*Pentanediacetic acid	0·344	*cyclo*Heptanediacetic acid	0·266
Dimethylglutaric acid	0·339	[Adipic acid	0·126]

Of equal importance with the figure of critical stability is the corresponding figure for the formation of the ring. It has elsewhere been indicated that these are by no means necessarily identical (Ingold, *loc. cit.*), a fact which, although made evident by a considerable amount of experimental testimony,‡ appears hitherto to have been largely ignored. Following the method previously used, it can be shown that the "formation-numbers," that is, the figures

† Compare Harries and Tank, *Ber.*, 1907, **40**, 4555.

‡ Thus there are numerous instances showing that although *cyclo*butane rings are much more difficult to close than *cyclo*propane rings, when once produced the former are actually more stable than the latter (Perkin and Simonsen, T., 1907, **91**, 817; Campbell and Thorpe, T., 1910, **97**, 2418).

representing the difficulty with which the closure of the ring is attended, are given with sufficient accuracy by the expression

$$\sin^2 \theta - 0{\cdot}29,$$

where θ has the same meaning as before. From this we obtain the following values :

Glutaric acid	0·43	*cyclo*Hexanediacetic acid	0·36
ββ-Dimethylglutaric acid *cyclo*Pentanediacetic acid	0·38	*cyclo*Heptanediacetic acid	0·35

In the present paper it is shown that, although the cyclic ketones are undoubtedly the products first formed when the calcium salts of the ββ-disubstituted glutaric acids are distilled, none of them survives the experimental conditions but is converted into an isomeric ketone or other product of ring fission. Consequently the figure for the critical stability governing this reaction must lie within the narrower range 0·266 to 0·126. On the other haud, there is no evidence of the formation of tetramethylene ketones from either glutaric or β-methylglutaric acid and it can be inferred that the critical formation number for such ketones is limited to the interval between 0·43 and 0·38.

Experimental.

Preparation of Substituted Glutaric Acids.

Glutaric acid was prepared by the oxidation of *cyclo*pentanone by means of dilute nitric acid (D 1·2) (Wislicenus and Hentzschel, *Annalen*, 1893, **275**, 309), β-methylglutaric acid by Day and Thorpe's method (T., 1920, **117**, 1465), and all the other acids by Guareschi's method (compare Kon and Thorpe, T., 1919, **115**, 686).

For the preparation of large quantities of material by the last method it has been found advantageous to work with 1½ gram-molecules of ketone at a time and to carry out the condensation in the cold : the reaction mixture contained in a wide-mouthed, stoppered bottle is left in a freezing mixture for some hours and then at the ordinary temperature, instead of being kept at 40°.

Except in the cases of diethyl ketone and suberone (Day, Kon, and Stevenson, T., 1920, **117**, 644), the contents of the bottle become solid, the reaction being completed after twenty-four to forty-eight hours.

The solid is purified by grinding with ether, dissolved in hot water (about 1½ litres), and the solution acidified, precipitating the imide. The yields are good, reaching 75 per cent. of the theoretical in some cases.

For the hydrolysis Thole and Thorpe's method (T., 1911, **99**, 422) was used and gave excellent results.

*Preparation and Distillation of Calcium Salts.**

Of the several methods tried, that described below was found to give the best results and was adopted as the standard for all the acids examined.

One gram-molecule of the acid is dissolved in dilute ammonia, the excess of ammonia boiled off and the solution poured on a paste made by slaking 100 grams of calcium oxide (this is a considerable excess). The mixture is thoroughly stirred, evaporated to dryness on a steam-bath, and the salt powdered and well dried at 100°. The powder is divided into twelve portions, and these are subjected to distillation in a stream of nitrogen in the apparatus described by Day, Kon, and Stevenson (*loc. cit.*).

The distillate is separated from a small amount of water which always collects, dried over calcium chloride, and fractionated.

I. *Acids containing a Quaternary Carbon Atom in the β-Position.*

ββ-Dimethylglutaric Acid.

The yield of distillate from a gram-molecule of this acid was usually 70 to 80 grams. The distillate was quite transparent and of a dark amber colour.

Result of fractionation:

(1) below 100°	19·4 grams	(3) 140—190°	4·8 grams
(2) 100—140°	3·8 „	(4) 190—250°	42·0 „

On progressive fractionation, the following compounds were isolated:

(1) *Acetone.*—This was identified by the boiling point and the formation of the semicarbazone melting at 187° (Found: N=36·74. Calc., N=36·48 per cent.).

The yield of acetone was about 17 grams, or 30 per cent.

(2) *Mesityl Oxide.*—This was contained in the second fraction and 2 grams (5 per cent.) of rather indefinite b. p. were isolated; the compound was identified by its semicarbazone (m. p. 162° [decomp.]) (Harries and Kaiser, *Ber.*, 1899, **32**, 1339), which was directly compared with a specimen prepared in the usual way (Found: N=27·28. Calc., N=27·08 per cent.).

(3) iso*Phorone* (VI).—The third and the fourth fractions contained this ketone, which was not accompanied by any other compound. It was isolated by means of its semicarbazone, which, when purified by repeated crystallisation from alcohol, was

* Barium salts were found to give the same results as calcium salts, without noticeable difference in yield; lead salts were unsatisfactory.

obtained in fine plates melting at 190—191° (Crossley and Gilling, T., 1909, **95**, 19). The semicarbazone was identified by direct comparison with a specimen prepared from the ketone obtained by Knoevenagel's method (*Annalen*, 1897, **297**, 113) (Found: C=61·42; H=8·83; N=21·98. Calc., C=61·51; H=8·77; N=21·53 per cent.).

The ketone regenerated from the semicarbazone by treatment with oxalic acid and steam distillation had the following properties:

b. p. 212°/763·5 mm. *; $d^{22\cdot0}$ 0·91985; $n_{D}^{22\cdot0}$ 1·47613;

whence $[R_L]_D$ 42·35, which is in good agreement with the figures found by Knoevenagel, as recalculated by Auwers and Eisenlohr (*J. pr. Chem.*, 1910, [ii], **82**, 129).

On treatment with hydroxylamine under the conditions described by Bredt and Rübel (*Annalen*, 1898, **299**, 170), an oxime was obtained, which on repeated crystallisation from ether and light petroleum could be separated into two forms, melting respectively at 79° and 102° (Wolff, *Annalen*, 1901, **322**, 380). In accordance with the observation of Kerp and Müller (*Annalen*, 1898, **299**, 220; 1896, **290**, 140) these oximes gave high results when analysed for nitrogen (Found: N=10·60, 10·62. Calc., N=9·14 per cent.).

The yield of *iso*phorone is about 45 grams, or 33 per cent.

(4) The formation of an unsaturated hydrocarbon was demonstrated by passing the gaseous products of the reaction through a U-tube cooled by means of liquid air. The liquid condensed in this way contained much acetone and a hydrocarbon which volatilised when the temperature of the mixture was allowed to rise. The hydrocarbon was passed into bromine and on removing the excess of the latter a heavy liquid was obtained, which was distilled. The portion boiling at 148—150° consisted of *iso*butylene dibromide, as it gave on heating with water in a sealed tube the odour of *iso*butaldehyde (Eltekoff, *Ber.*, 1878, **11**, 990) (Found: Br=73·29. Calc., Br=74·04 per cent.).

ββ-*Diethylglutaric Acid.*

Only one experiment was carried out with this acid, in which 1·2 gram-molecules (226 grams) were used. The yield of wet distillate was 109 grams. Result of fractionation:

(1) below 100°	22·3 *grams*	(5) 190—220°	10·6 grams
(2) 100—140°	11·3 ,,	(6) 220—280°	17·7 ,,
(3) 140—165°	10·2 ,,	Residue	8 ,,
(4) 165—190°	22·6 ,,		

* Pure naphthalene boils at 215° under similar conditions.

From the fraction of lowest b. p. two compounds were isolated by refractionation and treatment with water.

(1) *Acetone.*—This was separated from the other constituent of the mixture owing to its solubility in water and identified by means of the semicarbazone melting at 187°. The yield of acetone appeared to be about 12 grams, or 16 per cent.

(2) β-*Ethyl*-Δ^{α}-*butylene*, $CEt_2{:}CH_2$.—The oil remaining after the acetone had been removed was carefully dried and fractionated with the aid of a short column. After two distillations it boiled at 67—68° as a colourless, mobile liquid with a slight odour of garlic (Found: C=85·14; H=14·18. C_6H_{12} requires C=85·60; H=14·40 per cent.). Physical properties: $d^{20·5}$ 0·69403, $n_D^{20·5}$ 1·40276, whence $[R_L]_D$ 29·55. Calc. for C_6H_{12}, 29·44.

When the hydrocarbon was treated with bromine in chloroform solution two atoms of the halogen were taken up. The resulting *dibromide* boiled at 108—110°/50 mm. and possessed a pleasant, camphoraceous odour. On heating with water in a sealed tube for several hours, this yielded an *aldehyde*, recognised by the silver-mirror test, thus confirming the constitution of the hydrocarbon.

(3) *Diethyl Ketone.*—This compound was isolated from the portions of the distillate boiling between 100° and 140° in the form of its characteristic semicarbazone, which forms glistening, flattened needles melting at 139°. It was identified by direct comparison (Found: N=29·70. Calc., N=29·35 per cent.). The amount formed appears to be about 5 grams, or 5 per cent.

(4) On refractionating the third, fourth, and fifth fractions a very considerable portion of the distillate boiled between 160° and 190°. The weight of this fraction was 38 grams, corresponding with a yield of 25 per cent. It consisted of a *ketone*, $C_8H_{14}O$, to which the constitution V was assigned. The fraction, b. p. 160—190°, was treated with semicarbazide acetate and the *semicarbazone* collected and purified by rubbing with light petroleum. It was very soluble in most organic solvents and difficult to purify; it crystallised best from a mixture of ethyl acetate and light petroleum (b. p. 60—70°), from which it separated in silky, flattened needles melting at 145—146° (Found: N=23·13. $C_9H_{17}ON_3$ requires N=22·93 per cent.).

The existence of a more fusible modification of this semicarbazone could not be definitely established. The ketone reacted also with semicarbazide hydrochloride, although very slowly; the compound obtained was identical with the one described above.

The ketone regenerated from the semicarbazone by means of oxalic acid was a colourless liquid with a characteristic odour reminiscent both of *iso*phorone and mesityl oxide and boiling at

164—166°/759 mm. (Found: C=75·86; H=11·19. $C_8H_{14}O$ requires C=76·13; H=11·18 per cent.). Physical properties: $d^{18·9}$ 0·85444; $n_D^{18·9}$ 1·44241; whence $[R_L]_D$ 38·83. Calc. for $C_8H_{14}O|^{\prime\prime}$, 38·72.

The *oxime* of the ketone was prepared by warming it with hydroxylamine hydrochloride and sodium carbonate in alcoholic solution for one hour. On removing the alcohol by evaporation, the oxime separated as a colourless oil, which was taken up in ether and purified by distillation. It boiled at 118—119°/19 mm. and did not solidify when cooled in a freezing mixture (Found: N=9·76. $C_8H_{15}ON$ requires N=9·92 per cent.).

The catalytic reduction of the ketone $C_8H_{14}O$ to the compound $CHEt_2·CH_2·COMe$ by means of colloidal palladium and hydrogen was found to proceed very sluggishly and incompletely, and although the treatment was repeated three times the product still reduced permanganate. After being purified by shaking with a solution of the latter reagent, the new *ketone*, $C_8H_{16}O$, was isolated in the form of its *semicarbazone*, which melted at 141—142°. It crystallised from a mixture of ethyl acetate and light petroleum (b. p. 60—70°) in silvery plates or from methyl alcohol in long, flattened needles (Found: C=58·37; H=10·27. $C_9H_{19}ON_3$ requires C=58·34; H=10·34 per cent.). It appeared to be less soluble than the semicarbazone of the unsaturated compound.

(5) The fraction of highest b. p. obtained in this experiment was distilled under ordinary pressure, and several fractions were collected. The most important was that boiling between 240° and 260°.

The composition of this fraction approximates to that required by the formula $C_{11}H_{18}O$ (Found: C=79·51; H=10·49. Calc., C=79·47; H=10·90 per cent.), but a definite substance has not, as yet, been isolated from it, as a crystalline oxime or semicarbazone could not be obtained.

cyclo*Pentanediacetic Acid.*

The yield of the distillate, which was dark green in colour, was usually about 90 grams.

Result of fractionation:

(1) below 100°	12·5 grams	(4) 210—250°	12·0 grams
(2) 100—160°	5·9 ,,	(5) 250—320°	24·0 ,,
(3) 160—210°	21·2 ,,		

On progressive fractionation, 16 grams of liquid boiling below 100° were obtained and about 27 grams boiling between 160° and 210°.

The lowest fraction was separated into two constituents by shaking with water, exactly as described in the foregoing case (see p. 821).

(1) *Acetone* was identified as before by its boiling point and the formation of the semicarbazone. Yield about 12 grams, or 20 per cent.

(2) Methylene*cyclo*pentane (VII).—The portion insoluble in water, which amounted to about 4 grams, boiled, after careful drying, between 70° and 82° and consisted of the above hydrocarbon. On refractionation, this was obtained as a mobile, colourless liquid with a penetrating odour resembling that of garlic and having the following properties: $d^{20\cdot0}$ 0·7905; $n_D^{20\cdot0}$ 1·44070; whence $[R_L]_D$ 27·41, in good agreement with the figures given by Wallach (*Annalen*, 1906, **347**, 325) (Found: C=87·39; H=11·81. Calc., C=87·70; H=12·30 per cent.). The substance was further identified by the formation of the nitrosochloride melting at 82°.

(3) From the fraction, b. p. 100—160°, a little *cyclo*pentanone was isolated and recognised by the formation of its semicarbazone melting and decomposing at 205—206° (Wallach, *Annalen*, 1906, **347**, 326) (Found: N=29·95. Calc., N=29·76 per cent.).

(4) The large middle fraction, on redistillation, yielded nearly 20 grams of an oil boiling between 178° and 188° and consisting of cyclo*pentenylacetone* (III); this substance can also be recovered in considerable quantity from the fractions, b. p. 160—178° and 188—210° respectively, by means of semicarbazide.

The ketone was obtained in the pure state through its semicarbazone, although this proved to be an extremely tedious operation.

The *semicarbazone* is readily produced, and consists of a mixture of two forms. It is first purified by drying on porous plates and rubbing with light petroleum to remove oily impurities. Rubbing with ether, as recommended by Wallach for the separation of the two semicarbazones of *cyclo*hexenylacetone (*loc. cit.*), is unsatisfactory, as both forms dissolve to some extent; repeated crystallisation from methyl alcohol was found to be the best method. The less fusible form, when fairly pure, is but sparingly soluble in alcohol, although mixtures dissolve easily in a small quantity of the solvent; also, the less fusible form, which tends to separate first, is present in small quantity, thus adding to the difficulty of purifying the compound.

The less soluble form separates from methyl or ethyl alcohol in fan-shaped aggregates of needles melting and decomposing at 189° (Found: C=59·85; H=8·54; N=23·56. $C_9H_{15}ON_3$ requires C=59·64; H=8·34; N=23·19 per cent.).

The more soluble form separates from ethyl alcohol or benzene

in rosettes of small crystals melting at 138° (Found : N=23·44 per cent.).

An experiment was made to ascertain whether the two semicarbazones were derived from the same ketone. It was found that the ketone obtained from the pure compound melting at 189° still gave a mixture of the two forms on treatment with semicarbazide.

The ketone can be easily regenerated by boiling the semicarbazone with aqueous oxalic acid and isolated by distillation in steam.

It is a colourless liquid boiling at 181—184°/760 mm. The odour is strong and not very pleasant, somewhat resembling that of amyl acetate. The physical properties are : $d^{24\cdot3}$ 0·9294 ; $d^{19\cdot4}$ 0·9332 ; $n_D^{24\cdot3}$ 1·46500, $n_D^{19\cdot4}$ 1·46728 ; whence $[R_L]_D$ 36·91. Calc. for $C_8H_{12}O|$, 36·61 * (Found : C=77·09 ; H=9·91. $C_8H_{12}O$ requires C=77·37 ; H=9·85 per cent.).

*cyclo*Pentenylacetone is fairly readily reduced to *cyclopentylacetone*, $C_5H_9\cdot CH_2\cdot COMe$. The ketone (10 grams) was mixed with 5 c.c. of a 10 per cent. solution of palladium chloride, 5 c.c. of 10 per cent. gum arabic solution, 10 c.c. of water, and enough alcohol to give a clear solution. The mixture was shaken in an atmosphere of pure hydrogen maintained under a pressure of about 1800 mm. for six hours.

At the end of that time no further absorption seemed to occur. The ketone was isolated and converted into the *semicarbazone*, which was purified by crystallisation from ethyl acetate, from which it separated in glistening plates melting at 171—171·5° after several crystallisations ; from methyl alcohol it separated in long, flattened needles (Found : N=23·06. $C_9H_{17}ON_3$ requires N=22·93 per cent.). The ketone regenerated from this semicarbazone was a perfectly colourless liquid boiling at 179°/768 mm. and possessing an agreeable, intense odour resembling that of amyl acetate. Its physical properties were : $d^{20\cdot0}$ 0·9022 ; $n_D^{20\cdot0}$ 1·44452 ; whence $[R_L]_D$ 37·15. Calc. for $C_8H_{14}O$, 37·01 (Found : C=75·92 ; H=11·33. $C_8H_{14}O$ requires C=76·13 ; H=11·18 per cent.).

The reduced ketone is stable to permanganate in the cold.

(5) The fraction of highest b. p. was usually obtained as a deep blue, oily liquid. Its colour disappeared on reduction with palladium and hydrogen, although the composition of the oil appeared to remain unchanged. On distillation under reduced pressure, it did not boil very constantly, the greater part passing over at about 140—142°/11 mm. The composition of this fraction agrees with the formula $C_{16}H_{22}O$, so that it is probably derived from the condensa-

* The molecular refractivity of this ketone is unaccountably high, although scarcely as high as would be expected in the conjugated system $>C:CH\cdot CMe:O$ (compare footnote on p. 814).

tion of two molecules of *cyclo*pentenylacetone with the elimination of a molecule of water (Found: C=82·98; H=9·65. $C_{16}H_{22}O$ requires C=83·40; H=9·64 per cent.). Up to the present a crystalline compound with semicarbazide or hydroxylamine has not been obtained.

cyclo*Hexanediacetic Acid.*

The yield of distillate from this acid was usually about 96 grams. Result of fractionation:

(1) below 100°	10·8 grams	(4) 180—230°	33·1 grams
(2) 100—120°	5·6 ,,	(5) 230—290°	8·7 ,,
(3) 120—180°	17·1 ,,	(6) 290—350°	12·7 ,,

(1) On progressive fractionation, about 8 grams of a liquid, boiling below 60°, were obtained from the fraction of lowest b. p.

The liquid possessed the characteristic properties of acetone; this was confirmed by the formation of the semicarbazone melting at 187° (Found: N=36·73. Calc., N=36·48 per cent.). The yield of acetone was usually 12—15 per cent.

(2) The next definite fraction boiled between 100° and 110°, after repeated rectification at 105—106°, and was a colourless, oily liquid with a characteristic smell. It consisted of pure methylene*cyclo*hexane (VIII) (Found: C=87·45; H=12·41. Calc., C=87·50; H=12·50 per cent.).

Its physical properties were found to be as follows: $d^{20\cdot1}$ 0·80596; $n_D^{20\cdot1}$ 1·45153; whence $[R_L]_D$ 32·14 (calc., 31·81), in good agreement with the figure quoted by Wallach (*Annalen*, 1906, **347**, 329).

The identity of the substance was established by preparing the nitrosopiperidide by the method recommended by Favorsky and Borgmann (*Ber.*, 1907, **40**, 4867). This derivative was readily obtained, although in poor yield, and melted on crystallisation from 50 per cent. alcohol at 126·5—127° (Found: N=13·33. Calc., N=13·33 per cent.).

The hydrocarbon was oxidised by an ice-cold, alkaline, 1 per cent. solution of potassium permanganate (compare Wallach, *loc. cit.*). The glycol, $C_7H_{14}O_2$, obtained melted at 77·5° and crystallised very well from a mixture of ether and light petroleum in long, thin needles or from ether with a little methyl alcohol in large, transparent plates (Found: C=64·25; H=10·84. Calc., C=64·57; H=10·84 per cent.).

The yield of hydrocarbon appears to vary according to the conditions of the experiment and increases at the expense of the ketonic fraction if the experiment is conducted without passing nitrogen through the apparatus; it is usually about 11 per cent.

(3) *cyclo*Hexenylacetone (II) formed the greater part of the distillate and was contained in the portion boiling between 180° and 230°. The amount of this fraction was 42 grams, representing a yield of more than 30 per cent., but it did not boil very constantly, and the ketone could only be obtained from it by a tedious method of purification. Both the sodium hydrogen sulphite and the semicarbazide methods can be used, but the latter is preferable.

The semicarbazone is readily obtained, but it is very caseous in nature and consists of two forms, as in the case of the lower homologue (see p. 823). The two forms can be separated by rubbing the mixture with ether in accordance with the observation of Wallach. The residue, on repeated crystallisation from methyl alcohol and finally from benzene, is obtained in long, flattened needles, which lose their silky lustre on exposure and melt at 145° (Found: N=21·58. Calc., N=21·53 per cent.).

The compound also crystallises well from ethyl alcohol or ethyl acetate, but it is rather freely soluble in these solvents and especially so in chloroform. Dilute alcohol is not to be recommended, as the compound often separates from it in an amorphous form.

The ether extract, obtained as above, contains the more fusible form, which can be isolated by removing the ether, rubbing the residue with light petroleum, and crystallising repeatedly first from methyl alcohol and finally from benzene. It is thus obtained in flattened needles melting at 136—137° and closely resembling the foregoing compound in appearance (Found: C=61·67; H=8·92; N=21·65. Calc., C=61·51; H=8·77; N=21·53 per cent.).

Both forms were directly compared and found to be identical with the corresponding compounds obtained by Wallach's method.

When regenerated from the semicarbazone by means of oxalic acid, the ketone is obtained as a perfectly colourless oil with a pleasant odour reminiscent of amyl acetate and acetoacetic ester. It boils at 202°/754 mm. (pure naphthalene boils at 215° under similar conditions) and has the following physical properties $d^{24 \cdot 1}$ 0·9304; $n_D^{24 \cdot 1}$ 1·46867; whence $[R_L]_D$ 41·34, in good agreement with Wallach's figure (41·32) (Found: C=78·04; H=10·23 Calc., C=78·20; H=10·21 per cent.).

The oxime of *cyclo*hexenylacetone is a liquid, as found by Wallac[h] (Found: N=9·29. Calc., N=9·15 per cent.).

(4) The fraction of highest b. p., of which about 15 grams we[re] obtained, was an amber-coloured oil with a faint smell. It boile[d] for the most part at about 175°/11 mm., but the analytical figur[es] obtained (Found: C=82·48, 82·70; H=9·58, 9·63 per cent.) d[id] not lead to any definite formula and, as a solid derivative was [n]

formed with semicarbazide, the investigation of the substance was not continued.

cyclo*Heptanediacetic Acid.*

Only a quarter of a gram-molecule (55 grams) of this acid was available. The yield of distillate was 24 grams.

Result of fractionation :

(1) below 120° .... 1·1 grams	(5) 240—300° .... 3·7 grams
(2) 120—150° .... 2·5 „	(6) Residue distilled under reduced pressure .... 5·0 „
(3) 150—190° .... 3·2 „	
(4) 190—240° .... 5·9 „	

(1) On redistillation, only a small amount was found to boil at about 60° and this fraction was identified as acetone by its semicarbazone.

(2) The second fraction increased to about 4 grams on progressive fractionation, the major part boiling at 135—140°. This consisted of a hydrocarbon, but was still impure (Found : C=86·18; H=11·63. C_8H_{14} requires C=87·20; H=12·80 per cent.). An attempt was therefore made to identify it by oxidation, but it was unfortunately lost owing to an accident. In smell and other properties the compound resembled methylene*cyclo*hexane, and consisted, without doubt, of Wallach's methylene*cyclo*heptane (*Annalen*, 1900, **314**, 158; 1906, **345**, 146).

(3) Fractions (3), (4), and (5) were treated with an excess of semicarbazide acetate in aqueous alcoholic solution. The semicarbazone was precipitated by adding water after four days and purified by drying on porous plates, grinding first with light petroleum, and then with a mixture of light petroleum and ether.

The *semicarbazone* crystallises well from methyl alcohol in spherical clusters of needles, melting at 166·5—167° (Found: N=20·25. $C_{11}H_{19}ON_3$ requires N=20·09 per cent.).

The compound also occurs in a more fusible form, but the quantity of this appears to be small. It melts with sudden decomposition at 96°.

The ketone, cyclo*heptenylacetone* (IV), regenerated from the semicarbazone in the usual way, was obtained as a colourless liquid closely resembling *cyclo*hexenylacetone in its properties. It boiled at 223—225°/776 mm. (pure naphthalene boiled at 216·5° under the same conditions) and had $d^{23\cdot3}$ 0·9396, $n_D^{23\cdot3}$ 1·47917, whence $[R_L]_D$ 45·92. Calc. for $C_{10}H_{16}O|^{\prime\prime}$, 45·82 (Found : C=78·50; H=10·72. $C_{10}H_{16}O$ requires C=78·90; H=10·58 per cent.).

(4) The least volatile fraction was distilled under reduced pressure and a fraction boiling at 196—198°/11 mm. was collected. This appeared to be entirely analogous to the least volatile fraction

obtained from *cyclo*hexanediacetic acid, but so far its constitution has not been definitely settled (Found: C=82·83; H=10·32 per cent.).

2. *Acids Having a Free Hydrogen Atom attached to the β-Carbon Atom.*

Glutaric Acid.

The acid yielded under standard conditions 26 grams of distillate. This had a sweet, incense-like smell and gave on fractionation the following result:

(1) below 80°	2·7 grams	(5) 220—260°	4·1 grams
(2) 80—100°	1·9 ,,	(6) 260—320°	4·1 ,,
(3) 100—160°	1·6 ,,	Residue	7·0 ,,
(4) 160—220°	2·6 ,,		

On refractionating with a column the fractions (2) and (3) became still less, whereas a little more than 3 grams of a liquid boiling below 60° was obtained. This was identified as acetone by its odour and by the formation of its semicarbazone melting at 187°.

From the fraction (3), a very minute quantity of a semicarbazone was obtained on treating it with semicarbazide acetate and allowing to stand for three weeks. The semicarbazone could not be definitely identified, but gave, on treatment with a mineral acid, the characteristic odour of *cyclo*hexanone.

From the fractions (4) and (5) a small quantity of phenol was isolated on treatment with sodium hydroxide solution. The neutral oil which remained had no definite boiling point and did not react with semicarbazide and it appeared hopeless to attempt its identification.

β-Methylglutaric Acid.

The yield of distillate from a gram-molecule of this acid was about 42 grams (wet). The liquid was very dark and the smell incense-like and slightly phenolic.

Result of fractionation:

(1) below 100°	8·6 grams	(4) 200—250°	10·8 grams
(2) 100—140°	3·4 ,,	(5) 250—300°	5·2 ,,
(3) 140—200°	8·6 ,,	Residue	about 6 ,,

(1) On refractionating with a column, acetone (8 grams) wa obtained and identified by its semicarbazone. This correspond with a yield of 15 per cent. approximately.

(2) The next definite fraction obtained boiled between 100° an 130°, but amounted to not more than 2 grams. Repeated distill tion gave an oil with a sweet, camphoraceous odour, boiling mainl between 110° and 112°.

The analysis of the oil did not lead to a definite formula (Found: C=72·69, 73·36; H=11·11, 11·14 per cent.). When purified by repeated distillation it combined with semicarbazide to give a very soluble compound, which on repeated crystallisation from light petroleum (b. p. 60—70°) was obtained in iridescent plates melting at 105—106° (Found: N=29·01. Calc., N=29·35 per cent.).

This was proved to be the semicarbazone of methyl propyl ketone, as an admixture of this substance did not depress its melting point; when mixed with the *iso*propyl compound, the melting point was depressed nearly 20°.

(3) The fraction (3) yielded a certain amount of a semicarbazone when treated with semicarbazide acetate. It was found, however, that this consisted of a very soluble mixture, which on recrystallising three times from methyl alcohol formed clusters of flattened needles and melted at 174°. The ketone was regenerated from this before it was discovered that the semicarbazone was still contaminated with another compound. The ketone boiled somewhat indefinitely, the greater part at 170—175°, and on analysis gave numbers agreeing with the formula $C_7H_{12}O$ (Found: C=74·98, 75·24; H=10·75, 10·91. Calc., C=74·94; H=10·80 per cent.). Its physical properties approximated to those of inactive 3-methyl*cyclo*hexanone ($d^{20·8}$ 0·9124; $n_D^{20·8}$ 1·44853; whence $[R_L]_D$ 32·92. Calc., 32·34).

The ketone was therefore reconverted into the semicarbazone and this subjected to careful crystallisation from dilute methyl alcohol. The semicarbazone was finally obtained in glistening plates melting at 180—181°; it did not depress the melting point of the semicarbazone of 3-methyl*cyclo*hexanone, prepared from the synthetic ketone, which was also found to melt at the same temperature (Found: N=24·91. Calc., N=24·83 per cent.).

(4) Another semicarbazone was present in the mixture first obtained. It occurred in smaller quantity than the foregoing compound and accumulated in the mother liquors from the latter: it could only be separated with great difficulty. It melted at 156—158° after repeated crystallisation from dilute alcohol, but its crystalline form was somewhat indefinite (Found: N=23·44. $C_9H_{15}ON_3$ requires N=23·19 per cent.).

The corresponding ketone would therefore have the formula $C_8H_{12}O$, but it has not yet been obtained in sufficient quantity for identification.

(5) The fractions (4) and (5) were shaken with a 10 per cent. solution of sodium hydroxide, the aqueous extract separated from the oil, traces of oil removed by means of ether, and the liquid acidified. A copious precipitation of a phenolic substance occurred; this was taken up in ether and isolated in the usual manner. It

boiled between 200° and 210°, and gave on analysis figures in fair agreement with the formula C_7H_8O. Ferric chloride gave a violet colour with a solution of the substance, and it was identified as *m*-cresol by the formation of the tribromo-compound melting at 80—82° (Found: Br=69·88. Calc., Br=69·55 per cent.) and the trinitro-compound melting at 105—106°.

(6) The neutral oil which remained after the *m*-cresol had been dissolved was subjected to distillation; it boiled between 200° and 230° without giving any very definite fractions. It reacted very sluggishly and imperfectly with semicarbazide acetate; the semicarbazone melting at 156—158° was isolated in small quantity from the product. The investigation of this oil has been temporarily abandoned.

In conclusion, the author's best thanks are due to Prof. J. F. Thorpe, F.R.S., for his kind interest and advice during the progress of the investigation, and to Mr. J. N. E. Day and Mr. A. Stevenson for their help in the preparation of *cyclo*heptanediacetic acid.

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XCIII.—*Organic Derivatives of Silicon. Part XXV. Saturated and Unsaturated Silicohydrocarbons,* Si_4Ph_8.

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THE reactions which take place when diphenylsilicon dichloride is heated with sodium seem to be very numerous and are altogether unexpected. The halogen-free product is a complex mixture, from which, so far, three well-defined crystalline compounds have been isolated. The combined weights of these form less than 50 per cent. of the whole product and hitherto only two of them have been examined, except very superficially.

These two products are of particular interest because they seem to be isomeric and up to the present no satisfactory explanation of their relationship has suggested itself; even those constitutional formulæ which have been assigned to some of their derivatives must be taken as provisional.

The first product which will be considered is very sparingly soluble in cold benzene and in all the ordinary solvents and du

not melt at 300°; it is a silicohydrocarbon, Si_nPh_{2n}, and when first investigated it was believed to be a tetraphenylsilicoethylene, $SiPh_2:SiPh_2$, as it combined directly with iodine at the ordinary temperature.*

Quantitative experiments showed, however, that one molecule of the supposed tetraphenylsilicoethylene united with only one atom of iodine. The main, if not the only, product of the reaction was a crystalline iodide of the molecular formula $Si_4Ph_8I_2$. The most probable explanation of the facts now seemed to be that the supposed tetraphenylsilicoethylene was in reality a closed chain compound, $SiPh_2{<}{SiPh_2 \atop SiPh_2}{>}SiPh_2$. The fission of such a closed chain by the action of iodine at the ordinary temperature could not be dismissed as unlikely, because, since this would be the first known example of a molecule containing a closed chain of silicon atoms, there was no precedent which could act as a guide in the matter.

The hydrolysis of the crude iodide gave a mixture of at least four compounds; the principal product was a crystalline substance which, after a very long and careful examination, was thought to be a definite compound of the formula ${SiPh_2{\cdot}SiPh_2 \atop SiPh_2{\cdot}SiPh_2}{>}O$. The production of such an oxide from the di-iodide would obviously involve only normal reactions, since it is now known that even silicols of the type $SiR_3{\cdot}OH$ readily give the oxides $SiR_3{\cdot}O{\cdot}SiR_3$. It was not easy to decide from the results of analysis between the formulæ Si_4Ph_8O and $Si_4Ph_8(OH)_2$, but it seemed certain from a determination of its hydrogen value (p. 849) that the compound contained only one atom of oxygen (or two hydroxyl groups) combined with a chain of four directly linked silicon atoms. The fact that the compound decomposed slowly when it was heated at about 230° seemed to be incompatible with the formula Si_4Ph_8O, but otherwise the constitutions of the silicohydrocarbon, the di-iodide, and the oxide seemed to be fairly well established and represented respectively by the formulæ given above.

In the meantime, the examination of another of the crystalline products of the interaction of sodium and diphenylsilicon dichloride had made some progress. This substance differed from the "unsaturated" compound described above in very noteworthy respects. It was very readily soluble in cold benzene, and in various other

* Schlenk and Renning have described a substance which they represent by the formula $SiPh_2:CH_2$ (*Annalen*, 1912, **391**, 221) and which does not react with bromine (or with potassium permanganate in aqueous solution). Their elliptical method of preparation, however, does not inspire confidence, and the nature of their supposed unsaturated compound seems to be very doubtful.

solvents it dissolved freely; it was not acted on by iodine at the ordinary temperature, although it was attacked slowly by bromine, giving apparently a mixture of products. It formed well-defined crystals, and although it did not melt at 360°, its purity seemed to be fully established by microscopic examination. It will be referred to as the saturated silicohydrocarbon.

The results of analyses and cryoscopic experiments in benzene solution agreed with those required for the formula Si_4Ph_8; in other words, the two silicohydrocarbons, which differed so widely in their solubilities and in their chemical properties, appeared to be isomeric.

The existence of isomeric compounds, Si_4Ph_8, could not of course be accepted without further evidence; conceivable alternatives were considered, but all were contrary to the facts. The results of the silicon determinations alone seemed to offer sufficient proof that the two compounds were both silicohydrocarbons, since if either contained only one atom of oxygen to four $>SiPh_2$ groups the percentage of silicon would be 15·2 instead of 15·6. Even more conclusive evidence was afforded by determinations of their hydrogen values, which showed that the molecules of both the compounds contained no oxygen combined with the silicon atoms (compare this vol., p. 849).

If it be granted that the two substances are silicohydrocarbons, Si_nPh_{2n}, and there appears to be no alternative, the next question which arises is what are their molecular formulæ? The cryoscopic results obtained with the readily soluble saturated compound were very concordant and probably trustworthy; moreover, experiments made recently with the fairly complex silicohydrocarbons, diphenyldiethyldipropylsilicoethane, and dibenzyldiethyldipropylsilicoethane (this vol., p. 647) gave values which agreed closely with the calculated molecular weights; apparently therefore the saturated compound is undoubtedly Si_4Ph_8.

The molecular formula of the "unsaturated" silicohydrocarbon seemed to have been fully established by the conversion of this compound into the iodide, $Si_4Ph_8I_2$; but in view of the existence of the supposed isomeride, it was necessary to reconsider this conclusion.

The action of iodine might perhaps be compared with a pinacone condensation or with the change which occurs in the addition of halogen to a conjugated system,

$$SiPh_2{:}SiPh_2{,}SiPh_2{:}SiPh_2 + I_2 \longrightarrow SiPh_2I{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2I;$$

further observations seemed to show, however, that such a view could not be maintained. The "unsaturated" silicohydrocarbon

is very rapidly attacked by boiling tetrachloroethane,* giving apparently a dichloride, $Si_4Ph_8Cl_2$, corresponding to the di-iodide described above; at any rate, the product of the reaction is hydrolysed by water, giving the same compound as that obtained by the hydrolysis of the di-iodide, namely, the oxide, Si_4Ph_8O.

The final formation of this oxide seems to dispose of the possibility that the "unsaturated" compound might be after all a tetraphenylsilicoethylene.

At this stage determinations of the molecular weight of the "unsaturated" compound by the ebullioscopic method were made. The values obtained in benzene solution were about 700, which agreed well with the formula Si_4Ph_8, and were practically identical with those obtained by the cryoscopic method in the case of the supposed isomeric saturated compound.

Even if these results are discarded altogether as untrustworthy, it does not seem reasonable to regard the "unsaturated" compound as

$$SiPh_2{<}{\genfrac{}{}{0pt}{}{SiPh_2}{SiPh_2}}{>} \text{ or } SiPh_2{<}{\genfrac{}{}{0pt}{}{SiPh_2{\cdot}SiPh_2}{SiPh_2{\cdot}SiPh_2}}{>}$$

if the saturated compound is an octaphenyl*cyclo*silicotetrane, owing to the manifold differences between the two compounds.

A final and apparently an uncontrovertible piece of evidence that the "unsaturated" compound is Si_4Ph_8 is afforded by the fact that when the di-iodide, $Si_4Ph_8I_2$, is treated in boiling xylene solution with excess of sodium it is converted, although not quantitatively, into the original "unsaturated" silicohydrocarbon; the formula $SiPh_2{:}SiPh_2$, therefore, is definitely disposed of.

In addition to the important differences between the two silicohydrocarbons which have been already mentioned, there are many others; thus the "unsaturated" compound is very readily acted on by boiling nitrobenzene, whereas the saturated compound crystallises from this solvent almost if not entirely unchanged. One of the products of the action of nitrobenzene on the unsaturated silicohydrocarbon is a crystalline compound of the formula $Si_4Ph_8O_2$. This compound is also present in very small proportions in the crude oxide, Si_4Ph_8O, obtained with the aid of tetrachloroethane aud also in the crude product of hydrolysis of the di-iodide. Possibly

* The surprising readiness with which the silicohydrocarbon is attacked by tetrachloroethane recalls the behaviour of certain hydrides of silicon which are acted on violently by chloroform and by carbon tetrachloride: but it does not seem to be possible that the "unsaturated" compound contains the group $\cdot SiPh_2H$ for many reasons, as, for example, the non-formation of hydrogen iodide during the preparation of the di-iodide and the observed hydrogen value of the silicohydrocarbon.

it is a kind of peroxide, $\begin{array}{l}SiPh_2{\cdot}SiPh_2{\cdot}O\\ \,|\qquad\qquad\quad\;|\\ SiPh_2{\cdot}SiPh_2{\cdot}O\end{array}$, but so far as it has been examined its behaviour does not support this view, and it seems more probable that its constitution is represented by the formula

$$\begin{array}{l}SiPh_2{\cdot}O{\cdot}SiPh_2\\ |\qquad\quad\;\;|\\ SiPh_2{\cdot}O{\cdot}SiPh_2\end{array} \quad \text{or} \quad SiPh_2{<}\begin{array}{l}SiPh_2{\cdot}O\\ SiPh_2{\cdot}O\end{array}{>}SiPh_2.$$

Its hydrogen value shows that the molecule contains 1 atom of oxygen to every two $\colon SiPh_2$ groups.

One of these formulæ, however, is wanted for another compound which has been obtained in small quantities in a great many different ways and which forms well-defined, characteristic, rhomboidal prisms. This substance is produced when the saturated silicohydrocarbon is oxidised with nitric acid, or treated with bromine and the product submitted to hydrolysis; it is also produced when the oxide, Si_4Ph_8O, is oxidised with nitric acid or treated with iodine in presence of moisture. The hydrogen value of this substance seems to prove that the molecule contains one atom of oxygen to every two $\colon SiPh_2$ groups, and its constitution is therefore probably represented by one of the oxide formulæ just given. The principal interest which is attached to this compound at the present time is that it is a decomposition product of both the silicohydrocarbons, and its formation is therefore some indication that these two compounds are related to one another.

To the question, What is this relationship? the experimental data provide no satisfactory answer.

One of the compounds, of course, may be regarded as an octaphenyl*cyclo*silicotetrane, but which? To represent the one as a closed-chain compound containing in its molecule two tervalent silicon atoms, or two quadrivalent silicon atoms with a free bond each, $-SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2-$, would be one way out of the difficulty, but such a suggestion does not commend itself in view of all the facts, and indeed, seems to have little meaning.

The unsaturated compound might conceivably have the constitution

$$SiPh_3{\cdot}SiPh{\colon}SiPh{\cdot}SiPh_3,\ SiPh_3{\cdot}SiPh_2{\cdot}SiPh{\colon}SiPh_2,\ \text{or}\ \begin{array}{l}SiPh_3\\ SiPh_3\end{array}{>}Si{\colon}SiPh_2,$$

but the formation of any one of these compounds from $SiPh_2Cl_2$ would seem to be highly improbable, even assuming the presence in the latter of $SiPh_3Cl$ and $SiPhCl_3$; further, if the "unsaturated" compound had one of these constitutions and the saturated compound was an octaphenyl*cyclo*silicotetrane, the formation of the rhomboidal oxide, $Si_4Ph_8O_2$, from both substances could not be accounted for. Direct experimental evidence against the first two of the three formulæ just given seems to be afforded by the hydrogen

values of the two silicohydrocarbons (compare p. 849); even more important is the fact that, so far as can be ascertained, both compounds give on hydrolysis with wet piperidine only diphenylsilicol and its condensation products.

Owing to the readiness with which diphenylsilicol is converted by bases into a mixture of four or more condensation products (Kipping, T., 1912, **101**, 2125) and the difficulty of isolating some of these compounds, it is not possible to affirm that these are the only products of the hydrolysis of the two silicohydrocarbons. It can be stated, however, that the piperidine solutions obtained by decomposing both silicohydrocarbons have been carefully examined for triphenylsilicol, and not a trace of this compound could be found; if it had been present in any appreciable quantity it could scarcely have escaped detection. It seems therefore that all the three formulæ given above must be excluded.

The behaviour towards iodine, the observed hydrogen value, the nature of the products of hydrolysis, and other evidence also exclude from consideration any formula such as

$C_6H_4{:}SiPh{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh{:}C_6H_4$ or

$$\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}{>}Si{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}Si{<}\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}$$

for either of the silicohydrocarbons, or, in fact, any formula other than Si_4Ph_8. It may be, therefore, that both compounds are octaphenyl*cyclo*silicotetranes, but that in the one the four silicon atoms are all in one plane, whilst in the other they form a tetrahedral configuration.

The further investigation of these compounds is in progress and the action of sodium on other silicon dichlorides is also being studied; it is hoped that the results will lead to definite conclusions as to the nature of the two silicohydrocarbons.

EXPERIMENTAL.

Action of Sodium on Diphenylsilicon Dichloride.

A great many experiments have been made on the interaction of these two substances under different conditions, using rather more than the quantity of sodium calculated for the proportion $2Na : SiPh_2Cl_2$.

When the two substances are heated together in the absence of any diluent, a reaction sets in as soon as the sodium begins to melt, and the metallic globules are rapidly coated with a blue crust; if the containing vessel (provided with an air condenser) is then vigorously shaken, a very considerable development of heat takes

place, and the interaction seems to be completed almost immediately, with the formation of a brown, granular mass, containing bright globules of the excess of metal.

In order to prevent the sudden rise of temperature which may occur under these conditions, the dichloride was diluted with 3—10 volumes of toluene or xylene. In some experiments small portions of the metal were added to the diluted dichloride at intervals, but as a rule the whole of the sodium was covered with toluene and the diluted dichloride was added to it in small quantities at a time. In either case, the reaction started as soon as the temperature had risen to the melting point of sodium and the globules of metal were gradually transformed into a deep blue powder; the heat generated by the interaction, after each addition of dichloride, was usually sufficient to keep the liquid at its boiling point during some minutes.

Soon after the reaction has commenced, colourless six-sided crystals (substance *A*) begin to separate and gradually increase in quantity, but when the liquid has been boiled during about fifteen minutes (after all the dichloride or sodium has been added) no further change is observed.

The halogen-free, toluene or xylene solution is finally cooled and filtered and the dark blue residue of sodium chloride and unchanged metal is extracted thoroughly with boiling toluene. The extract deposits crystals of the product (*A*) and from the mother-liquors small quantities of another crystalline product (*C*) and a glue-like substance are also obtained. The dark blue powder, treated with a mixture of alcohol and acetic acid, in order to remove the sodium, changes to a pale blue solid, which, on the addition of water, gives a colourless solution; suspended in the latter is a very small proportion of a colourless, flocculent substance (*D*).

The residue which is obtained when the original toluene or xylene filtrate is evaporated is a yellow, glue-like or resinous mass; when treated with cold acetone, most of it (*E*) dissolves very readily leaving a colourless powder, from which three crystalline compound have been isolated, namely, the product (*A*), which is only ver sparingly soluble in boiling toluene, a compound (*B*) which dis solves very freely in cold toluene, and traces of a substance (*C* which is even more sparingly soluble than (*A*).

The product (*A*) is referred to as the "unsaturated" silicohydr carbon; the yield is usually about 1—2 grams from 20 of the d chloride. The product (*B*) is called the saturated silicohydrocarbo the yield is about the same as that of (*A*). The product (*C*) (yie about 0·1 gram) and the product (*D*) (yield about 0·5 gram) ha only been very superficially examined.

The main product of the reaction, namely, the resinous portion (*E*) which is readily soluble in cold acetone, accounts for the remainder of the material. So far the evidence points to the conclusion that this resin is a mixture of saturated complex silicohydrocarbons.

Although the experimental conditions have been varied considerably as indicated above, no definite statement can yet be made as to whether such variations have any influence on the course of the reactions which occur between the metal and the dichloride.

"*Unsaturated*" *Silicohydrocarbon*, Si_4Ph_8.

The crystalline deposit (*A*) mentioned above usually consists for the most part of the "unsaturated" silicohydrocarbon, and it is principally this substance which separates from the boiling toluene solution during the treatment of the dichloride with sodium. The crude preparations invariably contain a small proportion of the much more sparingly soluble compound (*C*), which is removed only with considerable difficulty by fractional crystallisation from toluene or benzene. Since the compound (*A*) does not melt at 300°, conclusions as to its purity had to be based on the results of microscopic examination and on its behaviour towards solvents; there is little doubt, however, that preparations which were regarded as pure did in fact consist of one substance only. Silicon determinations and combustions were made with various samples (Found: Si=15·3, 15·6; C=79·0, 80·0; H=6·0, 5·7. $SiPh_2$ requires Si=15·6; C=79·0 H=5·5 per cent.). The hydrogen value (compare p. 849) agreed very well with this formula.

Cryoscopic determinations were out of the question, owing to the sparing solubility of the compound, but by the ebullioscopic method in benzene solution the values obtained were M=637, 699 (calc. for Si_4Ph_8, M=729·6). These results must only be taken as rough approximations.

The "unsaturated" silicohydrocarbon crystallises from boiling benzene in short, flat, well-defined prisms; when the crystals which have separated from a cold benzene solution are heated in a Bunsen flame on a knife blade, they burn with a series of bright flashes, and when heated on a watch glass over a small flame, they decrepitate so violently that they are scattered all over the glass.

Rough determinations gave about 335° as the melting point of the "unsaturated" silicohydrocarbon, so that it has a lower melting point than hexaphenylsilicoethane, and also than the saturated silicohydrocarbon. The fused substance crystallises when it is cooled, but if it is kept melted for a short time it solidifies to a transparent glue which is readily soluble in cold acetone and benzene.

The "unsaturated" silicohydrocarbon is almost insoluble in most of the common organic solvents at the ordinary temperature, but it is appreciably soluble in benzene and toluene; rough determinations showed that at 15·5°, 100 grams of benzene dissolved 0·21—0·22 gram of the substance and at about 80°, 1·72 grams. It is less readily soluble in benzene than hexaphenylsilicoethane, and the great differences in solubility between this "unsaturated" and the saturated silicohydrocarbon described later (p. 846) are difficult to understand in view of the supposed isomerism of the two compounds.

The "unsaturated" silicohydrocarbon dissolves comparatively easily in boiling aniline, benzyl alcohol, and phenol, but it seems to undergo some decomposition when the solutions are boiled during some time; its behaviour towards boiling tetrachloroethane and nitrobenzene is described later. It is not attacked appreciably by boiling aqueous alkalis, and only slowly by alcoholic solntions of sodium methoxide; on the other hand, it is decomposed by boiling wet piperidine with great rapidity. Aqueous oxidising agents do not seem to act on it except very slowly, doubtless owing entirely to its insolubility.

Action of Iodine on the "Unsaturated" Silicohydrocarbon.

The "unsaturated" silicohydrocarbon dissolved in benzene combines directly with iodine, and even at the ordinary temperature the reaction takes place very rapidly; hydrogen iodide is not evolved in absence of moisture. Owing to the slight solubility of the silicohydrocarbon only enough benzene was used to dissolve a small fraction of the compound, and the iodine was added in small quantities at a time until a permanent coloration was produced. In some of the experiments the solution was warmed at about 60°, merely to hasten the solution of the silicon compound; in others it was warmed only after the colour of the last portion of iodine had disappeared, and cooled again before the addition of more halogen. All the materials were dried and atmospheric moisture was excluded. At first weighed quantities of the two substance in the proportion $I_2:Si_2Ph_4$ were employed, but it was at onc obvious that the iodine was in large excess; when the iodine wa added much more cautiously, only about one-half of the abov proportion of halogen was required to give a permanent coloratio to the solution.

As examples of the accuracy with which such titrations can b carried out, the following data may be given: 1·1 grams of substan required 0·36 gram of iodine; 0·38 gram is the theoretical quanti

for the equation $2Si_2Ph_4+I_2=Si_4Ph_8I_2$. 1·17 Grams of silicohydrocarbon required 0·397 gram of iodine, the quantity calculated on the same basis being 0·41 gram. The silicohydrocarbon passes into solution in the form of its iodide and the complete disappearance of the sparingly soluble substance should coincide with the production of a permanent coloration. If the silicohydrocarbon *has been incompletely purified and contains even a very small* proportion of the product (*C*) referred to above, the latter remains undissolved, as it is not acted on by iodine and is almost insoluble in cold benzene.

Octaphenyldi-iodosilicotetrane, $Si_4Ph_8I_2$.

The benzene solution of the preceding iodide, evaporated to dryness under reduced pressure, gave a colourless or pale yellow, crystalline residue, which dissolved freely in warm chloroform; from this solution the iodide was precipitated on the addition of dry ether in colourless crystals, which were rapidly washed well with ether on a filter and then heated for a few minutes at 100° in a dry atmosphere. For analysis, a weighed quantity of the substance was hydrolysed with aqueous acetone containing a small quantity of ammonium hydroxide solution, and the iodide in the aqueous solution was estimated; a silicon estimation was also made with a sample of the pure iodide (Found: I=25·2, 25·7; Si=11·5. $Si_4Ph_8I_2$ requires I=25·8; Si=11·5 per cent.). A molecular weight determination in benzene solution by the cryoscopic method gave M about 900, the calculated value being 983.

Octaphenyldi-iodosilicotetrane turns pink and then yellowish-brown on exposure to light and moist air. It crystallises well from a mixture of ether and benzene in highly lustrous, very acute rhomboidal plates, which do not melt or undergo any visible change even at 250°. It is only very sparingly soluble in cold ether, but dissolves rather freely in cold benzene. When a sufficiently small proportion of benzene is used in preparing the di-iodide, massive crystals of the latter are deposited. Although relatively stable in the solid state, its solutions in benzene and ether soon turn brown on exposure to air and light, and when dissolved in acetone it gives a yellowish-brown solution immediately; even crystals left in the dark in a saturated solution in benzene undergo gradual decomposition.

Products of Hydrolysis of the Di-iodide.

For the study of its products of hydrolysis, the crude iodide was treated with an ammoniacal solution of acetone. No particular attention was paid at the time to the duration of this treatment,

or to the concentration of the ammonium hydroxide; these factors, however, possibly had an important influence on the nature of the results.

The solid, halogen-free, colourless material thus obtained was usually somewhat pasty at first, but it soon became hard and friable; when roughly dried and extracted with cold acetone, about 10—15 per cent. of some very soluble glue-like matter dissolved. The rest of the material—a crystalline powder, only very sparingly soluble in cold acetone—was submitted to fractional crystallisation from nearly all the common solvents, including mixtures of them in various proportions. The first definite result of such operations was the isolation of a relatively very small quantity of a compound which crystallised in well-defined, rhomboidal prisms, melting sharply at 221—222° (p. 844), and later on a second well-defined by-product was identified in the final mother-liquors (p. 844).

The main product of hydrolysis which then remained crystallised from nearly all solvents in microscopic needles; to the unaided eye, the preparations had that white, opaque appearance which is common to mixtures, but under the microscope they looked quite homogeneous. The melting points of such preparations were most indefinite and irregular; some samples sintered at 205—210° and melted completely at about 220°; others did not sinter until about 220° and melted gradually up to about 245° or occasionally as high as 250—260°. Further, the melted material was rather a jelly than a liquid, and stuck to the sides of the tube; when cooled it did not solidify readily, but slowly gave a white solid which melted at a much lower temperature than the original substance, in some cases below 190°, but not sharply.

The ill-defined melting point of any given sample varied with the rate of heating and with the coarseness of the crystals; a sample, for example, which did not melt at 225° would do so as the temperature slowly fell to 210°, and one and the same sample would melt at 210—220° or at 230—245°, according to the rate at which it was heated. It seemed possible from these observations that the material was a mixture of the oxide and the dihydroxide, or even of these two substances and open-chain condensation products of the latter. Whether it was or was not a pure substance, it was very difficult to say, but the results of analysis seemed to show that it was an octaphenylsilicanetetrane oxide of the constitution

$$\begin{matrix} SiPh_2\cdot SiPh_2 \\ SiPh_2\cdot SiPh_2 \end{matrix}\!>\!O$$

(Found: Si=15·5. Calc., Si=15·2 per cent.)

Combustions of the substance were not attempted, as it was so difficult to burn it, even over the blowpipe flame. Cryoscopic determinations in benzene solution gave M 692, 817, and 70

(calc., M=744). Of more importance than these results were those obtained for the hydrogen value of the compound, which seemed to prove conclusively that the molecule contains four $SiPh_2$ groups to one atom of oxygen, or to two hydroxyl groups. The formula $Si_4Ph_8(OH)_2$, which requires Si=14·9 per cent. and a hydrogen value of 88·2 (p. 849), seems to be excluded, because the substance crystallises unchanged from boiling acetic anhydride and does not lose water when it is heated at 220° during ten minutes or so. The readiness with which the di-iodide undergoes hydrolysis seems to show definitely that the two iodine atoms, and therefore the two hydroxyl groups in the primary product of hydrolysis, are directly united to silicon; the constitution of the substance in question seems therefore to be fairly well settled.

Octaphenylsilicotetrane oxide is very sparingly soluble in cold alcohol, acetone, glacial acetic acid, ether, and light petroleum, but it dissolves freely in cold benzene and chloroform. It may be conveniently recrystallised from mixtures of chloroform or benzene and acetone, from which it separates in microscopic needles.

From hot ethyl acetoacetate, nitrobenzene, or aniline, the compound crystallises in a much more satisfactory manner, in long, transparent prisms, which seem to be hexagonal in section and are often aggregated together, forming beautiful, lustrous rosettes. These crystals become opaque when they are warmed with acetone.

The oxide is slowly acted on by an acetone solution of sodium hydroxide with evolution of hydrogen. It is oxidised by nitric acid in glacial acetic acid solution, giving the rhomboidal oxide described later, and it is attacked by hydrogen bromide in acetic acid solution, giving this same compound. It is not acted on appreciably by boiling nitrobenzene or by tetrachloroethane, in which respects it differs markedly from the parent hydrocarbon.

The glue-like snbstance which is extracted from the products of hydrolysis of the iodide (see above), and which is readily soluble in cold acetone, can be obtained as a colourless powder which does not melt at 250°; it has not been further examined.

Hydrolysis of the Di-iodide with Aniline and Water.

The complex character of the material obtained by hydrolysing the iodide with aqueous ammoniacal acetone was probably due either to the use of excess of iodine in the preparation of the iodide or to some action of ammonia on the original product of hydrolysis.

A much less impure product was obtained by warming the pure iodide with an aqueous alcoholic solution of aniline, or by leaving it in contact with acetone during some hours and then adding a

slight excess of sulphurous acid. These preparations, when fractionally crystallised from various solvents, gave deposits which, excluding the most soluble fraction (compare p. 844), seemed to be homogeneous, although they showed the same irregular behaviour as the oxide described above, with which they seemed to be identical; it may therefore be concluded that the normal product of hydrolysis of the di-iodide is that compound of indefinite melting point having the composition Si_4Ph_8O.

Action of Tetrachloroethane on the "Unsaturated" Silicohydrocarbon.

The "unsaturated" silicohydrocarbon dissolves freely in hot tetrachloroethane, and when a sufficiently concentrated solution immediately cooled again the silicon compound is deposited in ill-defined, microscopic prisms; when, however, such a solution is heated at its boiling point for a minute or two, there is no separation of crystals when the solution is afterwards cooled. Solutions which have boiled during about three to five minutes give, when evaporated under reduced pressure, a colourless residue which is soluble in dry ether; the ethereal solution slowly deposits a small proportion of a crystalline product which melts at about 180° and is probably the dichloride, $Si_4Ph_8Cl_2$. The addition of a little water to the ethereal solution causes the gradual deposition of a colourless product of hydrolysis, and aqueous washings of the solution give an immediate and heavy precipitate on the addition of a solution of silver nitrate. When the product is fractionally crystallised, it gives fractions which, except the most soluble one, seem to be all the same, and identical with the product of hydrolysis of the di-iodide. It has the same highly indefinite melting point as the latter, and the evidence of the identity of the two preparations is that derived from a direct comparison of their crystals as deposited from various solvents; also from observations of the melting points of mixtures heated simultaneously with the separate substances.

Action of Boiling Nitrobenzene on the "Unsaturated" Silicohydrocarbon.

Apparently the relative stability of the "unsaturated" silicohydrocarbon towards aqueous oxidising agents is due entirely to its insolubility, as it is readily attacked by boiling nitrobenzene. When a small quantity of the compound is dissolved in about five times its weight of hot nitrobenzene and the solution is immediately cooled, microscopic prisms, apparently those of the original substance, are deposited; but if the solution is boiled during a minute or so, crystals do not separate from the cooled solution. The reaction

occurs with a considerable development of heat, and even when only about 0·5 gram of the substance is used the solution will continue to boil for a few moments without the further external application of heat; the liquid turns dark brown and a faint odour of carbylamine is noticeable.

The addition of 6—8 volumes of alcohol to the cold solution causes the slow deposition of lustrous crystals, but precipitation is very incomplete. The solution is therefore submitted to steam distillation; the distillate has a marked green colour, possibly due to the presence of nitrosobenzene. When all the nitrobenzene has passed over, the water is decanted and the viscous, brown residue is dissolved in boiling acetone; this solution gives first a crystalline deposit and then a brown resin which is freely soluble in cold acetone. The crude crystalline substance is very easily purified. The yield is only poor and barely amounts to 50 per cent. of the material taken; as the product seems to be unchanged by boiling nitrobenzene, it seems likely that the poor yield is due, not to the result of heating the solutions during too long a period (two to ten minutes), but to the simultaneous occurrence of two or more reactions. The by-products have not yet been examined, but judging from their solubility in cold acetone, it seems probable that they consist mainly of condensation products of diphenyl silicanediol.

Analyses of the crystalline substance gave Si=14·7 and 14·8 per cent., and cryoscopic determinations in benzene solution gave M=720. These results agree with those required for a compound $Si_4Ph_8O_2$ (Si=*14·9*; *M*=*761*) or $Si_4Ph_8(OH)_2$ (Si=*14·9*; *M*=*763*), but they are not very different from those required for a compound of the composition Si_4Ph_8O (Si=*15·2 per cent.*).

A distinction between the formulæ $Si_4Ph_8O_2$ and Si_4Ph_8O is, however, easily arrived at from measurements of the hydrogen value of the compound (p. 849), which show that if the molecule contains four $:SiPh_2$ groups, as indicated by the cryoscopic determinations, it also contains two atoms of oxygen directly linked to silicon; as there is no evidence that the molecule contains hydroxyl groups, its constitution may be represented by one of the formulæ already given (p. 833), bnt it is not easy to decide which.

The compound crystallises from cold acetone containing a little nitrobenzene in massive lustrous forms, which appear to be almost cubes to the unaided eye; from the same mixture it is also deposited in small pyramidal crystals which have a six-sided base, usually somewhat rounded at the opposite obtuse angles; under the microscope, some of these crystals look exactly like a longitudinal section through a thick-walled barrel. Long, highly lustrous prisms,

hexagonal in section, are also formed, and from warm acetone the compound separates in slender needles. The crystals become opaque when cold acetone is poured on to them or when they are warmed gently with their mother-liquor; this appears to be due to the very unequal corrosion of the crystal faces. The compound is readily soluble in cold benzene and chloroform, less so in ethyl acetate, rather sparingly in cold acetone and very sparingly in alcohol.

When heated rather quickly, the compound generally melted at about 245—246° fairly sharply, but the temperature depended on the rate of heating, and if the sample were first kept at about 220° during some minutes it then melted at about 235°; the liquefied substance crystallised very readily when it was cooled and then melted at about 190°, but not completely; this second melting point seems to be a constant and fairly definite one, which can be observed over and over again with one and the same sample. These observations indicate dimorphism; further, samples crystallised from a cold mixture of benzene and acetone, if plunged into a bath heated at 220°, immediately melted, then generally solidified again at once and melted for a second time at about 242—245° and for a third time at about 190°, as stated above. This oxide, $Si_4Ph_8O_2$, is present in small proportions in the final, most soluble fractions of the oxide, Si_4Ph_8O, whether the latter has been produced by the hydrolysis of the iodide in various ways (p. 842) or by the action of tetrachloroethane, followed by that of water, on the "unsaturated" silicohydrocarbon. It differs from octaphenylsilicotetrane oxide in one noteworthy respect; although it is oxidised by nitric acid in acetic acid solution, it does not seem to give the rhomboidal oxide described later. It does not behave like a peroxide and does not liberate halogen from a solution of hydrogen iodide in acetic acid.

The Rhomboidal Oxide, $Si_4Ph_8O_2$.

This substance was first observed during the examination of the earlier preparations of the oxide, Si_4Ph_8O (p. 840). It is easily recognised by its appearance under the microscope and it is readily separated from the oxide Si_4Ph_8O, because it is so much less soluble than the latter in chloroform, benzene, and other solvents.

The compound usually separates from ethyl acetate, chloroform, and benzene in rhomboidal crystals, but from these and other solvents it is also deposited in fern-like masses or in well-defined pyramidal crystals, having a rhomboidal base and often a truncated apex. It is apparently dimorphous; when precipitated from a warm benzene solution by the addition of acetone, it sometimes

separates in long needles, which form a bulky mass, but if left at the ordinary temperature in contact with their mother-liquor, these bulky needles give place to a compact deposit of the small rhomboidal prisms. The latter often become translucent or opaque when warmed with their mother-liquor, but sometimes remain quite transparent.

The *rhomboidal oxide* melts sharply at 221—222° to a clear liquid which solidifies immediately when it is cooled and melts again at 221—222°. The formula assigned to this substance is based chiefly on the results of silicon estimations and the hydrogen value; molecular-weight determinations were made by the ebullioscopic method, but very little weight can be attached to the results (Found: Si=15·1. Hydrogen value=59·7. M=800—900. $Si_4Ph_8O_2$ requires Si=14·9 per cent. Hydrogen value=58·3. M=761).

The hydrogen value alone does not exclude the formula $HO{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}OH$ (p. 849), but all the other evidence available points to one of the alternative closed-chain formulæ already given (p. 834). It is obvious that certain objections might be raised to all these formulæ, but it would not be profitable to discuss such matters at the present juncture.

The rhomboidal oxide is apparently isomeric with the compound formed from the "unsaturated" silicohydrocarbon by the action of nitrobenzene; it is certainly much less soluble than the latter in chloroform, benzene, and most other common solvents, but perhaps the difference is not greater than might be expected in the case of isomerides having the suggested relationship; the rhomboidal oxide is very prone to form supersaturated solutions, whereby a false impression of its solubility might be created. The rhomboidal oxide has been obtained, but always in relatively small quantities, both from the saturated and the "unsaturated" silicohydrocarbons. Thus, it is formed when the saturated compound is heated with glacial acetic acid containing a small proportion of nitric acid; also when the saturated silicohydrocarbon is treated with bromine at the ordinary temperature and the product submitted to hydrolysis. It has not been obtained directly from the "unsaturated" silicohydrocarbon, but it is formed when the oxide, Si_4Ph_8O, is cautiously oxidised with nitric acid in glacial acetic acid solution, or very carefully treated with piperidine in acetone solution. It is also produced by the decomposition of the iodide in benzene solution, probably owing to the combined action of atmospheric oxygen and hydrogen iodide.

None of these methods of formation throws much light on the structure of the oxide or on the relationship between the saturated and the "unsaturated" silicohydrocarbons; so far a good method

for its preparation has not been elaborated. Except for its decomposition under the influence of aqueous piperidine or methyl-alcoholic solutions of alkali hydroxides, the oxide seems to be relatively very stable; it crystallises unchanged from boiling acetic anhydride and it is only very slowly oxidised by an acetic acid solution of nitric acid.

Saturated Silicohydrocarbon, Si_4Ph_8.

The product (*B*) of the interaction of diphenylsilicon dichloride and sodium (compare p. 836) is easily obtained in a pure state by recrystallisation from ethyl acetate. It does not melt at 400°, but if kept at this temperature during a short time it is changed into a glue-like mass. As it crystallises in short, well-defined, rectangular prisms which are fairly characteristic, its purity could be relied on with practical certainty from its appearance under the microscope. Many different samples were analysed (Found: Si=15·5, 15·6, 15·8, 15·7, 15·8; C=78·3; H=5·6. $SiPh_2$ requires Si=15·6; C=79·0; H=5·5 per cent.). The hydrogen value showed clearly that the substance was a silicohydrocarbon (compare this vol., p. 849) and cryoscopic results in benzene solution gave M=734, 718, 718 (calc. for Si_4Ph_8, M=729·6).

This saturated silicohydrocarbon dissolves very readily in cold benzene; it is also readily soluble in cold chloroform and hot ethyl acetate, but only sparingly in boiling acetic acid and almost insoluble in cold acetone, ether, and ethyl alcohol. Compared with the "unsaturated" silicohydrocarbon, it is a very inert substance. It is not attacked appreciably by iodine in benzene solution at the ordinary temperature, and even bromine acts on it very slowly. It may be repeatedly recrystallised from boiling tetrachloroethane or boiling nitrobenzene without its undergoing any appreciable decomposition, and it may also be recrystallised from boiling piperidine several times without any notable change. When, however, its solution in wet piperidine is heated at about 90° during some hours, the silicohydrocarbon is completely decomposed; from the solution it is possible to isolate diphenylsilicanediol and tetra-anhydrotetrakisdiphenylsilicanediol (T., 1912, **101**, 2125), but no substances other than diphenylsilicanediol and its condensation products seem to be formed in this reaction. The silicohydrocarbon is also acted on, but relatively slowly, by aqueous methyl alcohol or acetone solutions of alkali hydroxides; from these solutions after the expulsion of the organic solvent, acetic acid precipitates long, colourless needles which have the (somewhat indefinite) properties of diphenylsilicanediol.

The action of bromine on a carbon tetrachloride solution of the

saturated silicohydrocarbon at the ordinary temperature does not result in the separation of any silica; so far the only products which have been identified are the rhomboidal oxide and condensation products of diphenylsilicanediol. When the saturated silicohydrocarbon, partly dissolved and partly suspended in boiling acetic acid, is treated with a small proportion of nitric acid, a vigorous action sets in, but soon subsides; after some time the crystalline deposit consists of the rhomboidal oxide either alone or mixed with a certain proportion of the unchanged silicohydrocarbon.

Formation of the "Unsaturated" Silicohydrocarbon from the Di-iodide.

A freshly-prepared benzene solution of the di-iodide was evaporated under reduced pressure and the residue dissolved in xylene; a considerable excess of sodium was then added and the solution was boiled during about nine hours until the separation of sodium iodide seemed to be at an end and a portion of the filtered liquid seemed to be free from halogen. When cold, the xylene solution was filtered and the residue extracted with boiling benzene; from the extract there was obtained a compound which, judging from its appearance under the microscope and its slight solubility in benzene, was identical with the "unsaturated" silicohydrocarbon; like the latter, moreover, it combined with iodine in benzene solution at the ordinary temperature and the iodide, on hydrolysis, gave a product which was indistinguishable from the oxide, Si_4Ph_8O, already described. The original xylene filtrate gave on evaporation a residue, which was treated with cold acetone; the insoluble portion consisted of the "unsaturated" silicohydrocarbon, whereas the soluble matter was a glue-like or resinous substance similar in character to the main product of the action of sodium on diphenylsilicon dichloride. As it seemed impossible that this glue contained any of the saturated silicohydrocarbon, it was not further examined. The yield of the "unsaturated" silicohydrocarbon was not more than 60—70 per cent. of the theoretical and the conversion of the iodide into this substance seemed to require a higher temperature and far more prolonged heating than are necessary in the preparation of the "unsaturated" compound from diphenylsilicon dichloride.

The authors desire to express their thanks to the Industrial and Scientific Research Department for assistance in connexion with this investigation.

UNIVERSITY COLLEGE,
NOTTINGHAM. [*Received, February 17th,* 1921.]

XCIV.—*Organic Derivatives of Silicon. Part XXVI. Piperidine as an Analytical Reagent.*

By Frederic Stanley Kipping and James Edwin Sands.

In the course of the investigation described in the preceding communication, difficulties arose in the determination of the molecular formulæ of some of the compounds. Silicon estimations as a rule gave trustworthy results when the compound was decomposed with a mixture of concentrated sulphuric and nitric acids, but sometimes the residual silica contained carbon which did not burn away even on prolonged and intense ignition; a similar but darker residue was often obtained when the silicon compound was heated alone, so that the results of combustions could not have been relied on. The quantity of carbon in the silica residues was sometimes estimated with the aid of hydrofluoric acid, but as the theoretical quantities of silicon calculated for two possible formulæ might differ by only about 0·2 to 0·3 per cent., this method was not sufficiently trustworthy.

In these circumstances some additional analytical method was urgently required, and an estimation of the hydrogen evolved by the action of alkalis on the silicon compound naturally suggested itself, this process having been used in these laboratories many years ago. Some of the substances, however, were not appreciably attacked by aqueous solutions of alkali hydroxides, and owing to their very slight solubility in alcohol or acetone, the presence of either of these solvents did not cause the reaction to proceed with suitable rapidity.

The behaviour of the silicon compounds towards various organic bases, such as pyridine, benzylamine, and piperidine, was then examined, and it was found that whereas the first two bases had a very slow action, piperidine brought about a rapid decomposition accompanied by an evolution of hydrogen.

Now if this action of piperidine was analogous to that of alkali and took place quantitatively, it would be very easy to distinguish between certain possible formulæ for a particular compound by measurement of the evolved hydrogen. The method was tested by making experiments with the "unsaturated" silicohydrocarbon described in the preceding paper. A small quantity of the substance (about 0·1 gram) is placed in a test-tube together with a small tube containing piperidine (about 2—3 c.c.) and the test-tube is connected to a long, graduated tube partly immersed in a cylinder of water. When the air in the apparatus has acquired

room temperature, the piperidine is brought into contact with the silicon compound and the reaction is started by the application of heat. A brisk evolution of hydrogen sets in, and after the liquid has been heated during ten to fifty minutes the operation is finished. A high degree of accuracy in measuring the volume of the gas is, of course, unnecessary.

The results were so satisfactory in the case of the "unsaturated" silicohydrocarbon (see below) that this method of analysis was applied to all the other compounds described in the preceding paper; it is very easily carried out and requires only a very small quantity of material. In some cases a little pyridine was added to the piperidine to see if the presence of a reducible substance would lower the results, but it did not. Experiments were also made with hexaphenylsilicoethane and *dl*-diphenyldiethyldipropylsilicoethane (this vol., p. 647), but after six hours' heating in the case of the former and twenty hours' heating in the case of the latter no hydrogen had been evolved; it seems therefore that a compound such as $SiPh_3{\cdot}SiPh{:}SiPh{\cdot}SiPh_3$ might give $SiPh_3{\cdot}SiPh(OH)_2$ on hydrolysis and not be further decomposed, in which case, of course, the hydrogen value would be much lower than that of the "unsaturated" silicohydrocarbon, Si_4Ph_8, which is hydrolysed in accordance with the equation

$$Si_4Ph_8 + 8H_2O = 4SiPh_2(OH)_2 + 4H_2.$$

Some of the formulæ discussed in the preceding paper, between which it was necessary to decide, are given in the following table, which shows the calculated percentage of silicon and also the volume of hydrogen which should be evolved by the decomposition of 1 gram of the compound; the latter is termed the hydrogen value, and the figures in the last column give the hydrogen values found experimentally.

Compound.		% Si.	Calculated. Hydrogen value. 1 mol.	1 gram.	Found. Hydrogen value.
"Unsaturated" silicohydrocarbon	S_4Ph_8	15·56	$4H_2$	123 c.c.	118, 119, 120 c.c.
Saturated silicohydrocarbon	S_4Ph_8	15·50	$4H_2$	123	120, 122
Octaphenylsilicotetrane oxide	$SiPh_2{\cdot}SiPh_2$ $SiPh_2{\cdot}SiPh_2$ >O	15·22	$3H_2$	90·3	87·5
Octaphenylsilicotetranediol	$SiPh_2{\cdot}SiPh_2{\cdot}OH$ $SiPh_2{\cdot}SiPh_2{\cdot}OH$	14·86	$3H_2$	88·2	—
Oxide $Si_4Ph_8O_2$	$SiPh_2{\cdot}SiPh_2{\cdot}O$ $SiPh_2{\cdot}SiPh_2{\cdot}O$	14·89	$2H_2$	69·0	59·7
Rhomboidal oxide $Si_4Ph_8O_2$	$SiPh_2{\cdot}O{\cdot}SiPh_2$ $SiPh_2{\cdot}O{\cdot}SiPh_2$	14·89	$2H_2$	59·0	59·4
Hexaphenylsilicotriane oxide	$SiPh_2{\cdot}SiPh_2$ $SiPh_2{\cdot}O$	15·1	$2H_2$	79·0	—
Hexaphenylsilicotrianediol	$HO{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}OH$	14·7	$2H_2$	77·0	—
Tetraphenylsilicoethanediol	$HO{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}OH$	14·2	H_2	56·0	—

It will be seen that the results obtained with the two silicohydrocarbons afford very strong evidence that both the compounds have the formula $(SiPh_2)_n$; that neither contains the group $\cdot SiHPh_2$, which would give three instead of two atoms of hydrogen, or a group $C_6H_4{:}SiPh\cdot$, which would give either one or three atoms of hydrogen, according to the course of the reaction. It also seems probable that if either substance contained a $\cdot SiPh_3$ group it would give a low hydrogen value (see above). The distinction between the formulæ Si_4Ph_8O and $Si_4Ph_8O_2$ or the formulæ Si_4Ph_8O and Si_3Ph_6O is also rendered a simple matter, whereas silicon estimations alone would have been insufficient.

The authors desire to thank the Industrial and Scientific Research Department for assistance in carrying out this work.

UNIVERSITY COLLEGE,
NOTTINGHAM. [*Received, February 17th,* 1921.]

XCV.—*The Use of Aluminium Chloride and Ferric Chloride in the Preparation of Phenolphthalein.*

By CHARLES FREDERICK WARD.

THIS paper contains an account of some attempts made early in 1920 to improve Baeyer's method for the preparation of phenolphthalein (*Ber.*, 1876, **9**, 1230; *Annalen*, 1880, **202**, 68), in which sulphuric acid is used as a condensing agent. The substances which were used as condensing agents in this research were anhydrous aluminium chloride, anhydrous ferric chloride, and acetic anhydride.

Anhydrous aluminium chloride gives an improved yield of phenolphthalein when the phthalic anhydride and aluminium chloride are in molecular proportions and the phenol is in slight excess. Only poor yields are obtained by using an excess of either phenol or aluminium chloride. The reaction is smooth and easily controlled by adjusting the temperature of the reacting mixture. The product is clean and is easily purified.

Anhydrous ferric chloride is not so satisfactory as aluminium chloride. The yields are poor and the products more difficult to purify, being contaminated with other condensation products, chiefly 1- and 2-hydroxyanthraquinones and 2-*o*-hydroxybenzoyl-

benzoic acid. The formation of fluoran was not observed in any of these experiments (see Copisarow, T., 1920, **117**, 209).

Acetic anhydride has no action as a condensing agent in the preparation of phenolphthalein by this method.

Experimental.

Aluminium Chloride.

(1) Phthalic anhydride (10 grams), phenol (25 grams), and anhydrous aluminium chloride (15 grams) were mixed in a 250 c.c. flask and gently warmed in an oil-bath. At about 45° a vigorous reaction set in, hydrogen chloride being evolved, and the whole mass changed to a bright pink liquid. The temperature was gradually raised to 100° during one hour, when the reaction was apparently completed, as hydrogen chloride was no longer evolved and the product had set to a solid mass. The product was distilled in a current of steam and the residue extracted first with dilute hydrochloric acid to remove alumina and then with dilute sodium hydroxide solution. The crude phenolphthalein was precipitated by dilute acid and crystallised from 70 per cent. methyl alcohol. The first fraction consisted of almost pure, well-crystallised phenolphthalein. A further quantity was obtained from the mother-liquors, which finally deposited a glue-like mixture of hydroxyanthraquinones and hydroxybenzoylbenzoic acid. The yield of phenolphthalein calculated on the phthalic anhydride taken was 35 per cent. of the theoretical.

(2) In this experiment, similar quantities were taken, but the heating was continued during five hours at 100°. The yield was again 35 per cent., so that the reaction is practically completed after one hour.

The results of several experiments are best summarised in the form of a table. Number 5 shows the quantities and conditions which gave the best result.

Phthalic anhydride, grams.	Phenol, grams.	Aluminium chloride, grams.	Period of heating, hours.	Yield, per cent.
10	25	15	1	35
,,	,,	,,	5	,,
,,	50	,,	5	20
,,	20	20	0·25	trace
,,	,,	15	1	40

The temperature in all cases was gradually raised from 40° to 100°, except in experiment 4, when the mixture set to a solid mass at 60° after fifteen minutes.

Ferric Chloride.

Phthalic anhydride (10 grams), phenol (20 grams), and anhydrous ferric chloride (20 grams, freshly prepared) were mixed and gently heated. No reaction was apparent, but after heating at 130° during five hours and treating the product as before, a yield of 30 per cent. of the theoretical was obtained after a tedious process of purification from other condensation products.

Other experiments showed that an excess of phenol had no influence on the yield of phenolphthalein and the results are summarised in the following table:

Phthalic anhydride, grams.	Phenol, grams.	Ferric chloride, grams.	Period of heating, hours.	Yield, per cent.
10	20	20	5	30
,,	25	25	,,	35
,,	50	20	,,	,,

The temperature in all cases was between 130° and 150°. The products were dark brown and could only be obtained pure after many crystallisations.

Acetic Anhydride.

In an experiment with acetic anhydride as the condensing agent, made in the hope of obtaining phenolphthalein diacetate, phenyl acetate was the only product of the reaction.

Addendum.

In March, 1920, while this work was in progress, Copisarow (*loc. cit.*) published a paper dealing with the condensation of phenols and phthalic anhydride in the presence of various condensing agents: boric acid and sulphuric acid, hydrogen chloride, zinc chloride (anhydrous), and hydrogen chloride. Phenolphthalein was obtained in 50 per cent. yield by the use of zinc chloride and anhydrous hydrogen chloride together as condensing agents and a method of purification similar to that employed in this research. As such a method is more economical, in addition to being more efficient, there was no object in continuing the present research.

CHEMICAL DEPARTMENT,
UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, May 4th*, 1921.]

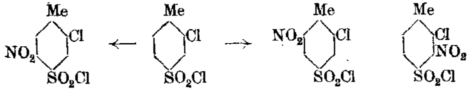
XCVI.—*The Cumulative Effect of the Chlorine Atom and the Methyl and Sulphonyl Chloride Groups on Substitution in the Benzene Nucleus. Part I.*

By WILLIAM DAVIES.

THE position taken up by a new, entering group under the directive influence of two groups already present in the benzene nucleus has been generalised in laws that have almost completely been established. When three groups are present, however, the problem where substitution will take place becomes more complicated, and no systematic attempt at its solution has been made. It was thought that the nitration of certain chlorotoluenesulphonyl chlorides would throw light on this problem.

The first part of the research is concerned with the constitution of the different mononitro-derivatives of 2-chloro-*p*-toluenesulphonyl chloride (I). The only literature on the subject is the mere statement in the German patent (D.R.-P. 145908; Friedländer, VII, 467) that 2-chloro-5-nitro-*p*-toluenesulphonyl chloride (II) is formed on nitration. No evidence of this is adduced.

Now it would at first sight be expected that the ortho-directing influence of the methyl group, together with the meta-directing influence of the sulphonyl chloride group, would be greater than the tendency, due to the chlorine atom, for substitution to take place in the para-position with respect to the chlorine atom. Therefore more of III would be expected than of II. The method of nitration and the analysis of the products are described in the experimental part of this paper.



(II.) (I.) (III.) (IV.)

The orientation of 2-chloro-5-nitro-*p*-toluenesulphonyl chloride presented considerable difficulties. Heating in a sealed tube with fuming hydrochloric acid for periods of from twelve to thirty-six hours between 140° and 180° resulted in the sulphonyl chloride group being converted into the sulpho-group, but led to no further hydrolysis. Similarly, when the sodium salt in 80 per cent. sulphuric

acid was distilled in superheated steam at 250°, no oil passed over into the distillate. The conversion into a dichloronitrotoluene was then attempted by the elimination of sulphur dioxide. However, careful heating at the ordinary and under diminished pressure led to extensive decomposition, and only a trace of sulphur dioxide was formed. Efforts to replace the sulphonyl chloride group by chlorine were made by heating with phosphorus pentachloride, after the method described by Olivier (*Rec. trav. chim.*, 1920, **39**, 502). Negative results were obtained.

Finally, the powdered sodium chloronitrotoluenesulphonate was gently heated separately with potassium ferrocyanide, sodium formate, and sodamide, in order to replace the sulpho-group by a cyano-, carboxyl, and amino-group respectively. However, the sodium chloronitrotoluenesulphonate, which decomposes at about 220°, deflagrated in all these cases before the reagents could enter into reaction.

Since II could not directly be converted into known derivatives, its constitution was determined by a circuitous method. Sodium chloronitrotoluenesulphonate was reduced and converted into 6-*chloro*-m-*toluidine*-4-*sulphonic acid* (V), which was converted into a chlorodibromotoluidine and sulphuric acid by the action of bromine water. This compound is undoubtedly 6-*chloro*-2 : 4-*dibromo*-m-*toluidine* (VI).

(V.) (VI.)

The replacement by bromine of the sulpho-group in aminobenzenesulphonic acids, through the action of bromine water, has been found to occur only when the amino- and sulpho-groups are in the ortho- or para-position with respect to each other (Bahlmann, *Annalen*, 1877, **186**, 309; Evans, P., 1896, **12**, 235). When these two groups are in the meta-position to each other, the action of bromine water leads to the formation of bromoaminobenzenesulphonic acids.

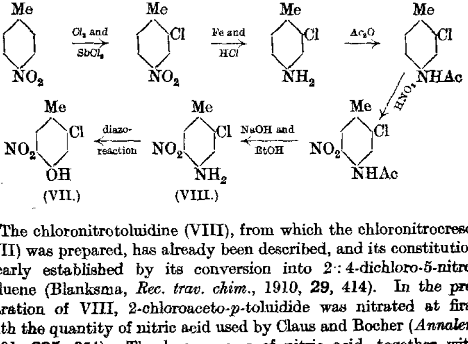
Therefore the conversion of the chlorotoluidinesulphonic acid in question into a chlorodibromotoluidine shows that the original chloronitrotoluenesulphonyl chloride is either II or IV.

This conclusion was borne out by the behaviour of the sodium chloronitrotoluenesulphonate when boiled with dilute sodium hydroxide solution. A red salt, almost insoluble in the boiling

solution, was gradually formed, and it was converted by acidification into a chloronitrocresol readily volatile in steam and possessing a faint smell recalling that of *o*-nitrophenol. Moreover, the alkali salts were intensely coloured. These properties show that the nitro-group in the chloronitrocresol is in the ortho-position with respect to the hydroxy-group, and therefore that the parent substance is either II or IV.

*2-Chloro-5-nitro-*p*-cresol* (VII), m. p. 71°, is of unusual interest because the *sodium* salt is sparingly soluble, whilst the *potassium* salt is moderately soluble in water. The sodium salt is readily formed as an amorphous red precipitate by double decomposition from the potassium salt. This reaction may be useful in estimating the amount of the sodium salt in a mixture of sodium and potassium salts.

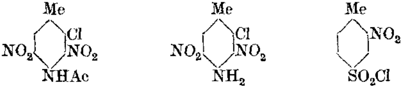
Since the chloronitrocresol melting at 71° might possibly have been derived from the third possible chloronitrotoluenesulphonyl chloride (IV), the substance having the formula VII was prepared by a method that left no doubt as to its constitution, and the two chloronitrocresols were compared. The diagram below summarises the reactions involved in the synthesis.



(VII.) (VIII.)

The chloronitrotoluidine (VIII), from which the chloronitrocresol (VII) was prepared, has already been described, and its constitution clearly established by its conversion into 2 : 4-dichloro-5-nitrotoluene (Blanksma, *Rec. trav. chim.*, 1910, **29**, 414). In the preparation of VIII, 2-chloroaceto-*p*-toluidide was nitrated at first with the quantity of nitric acid used by Claus and Bocher (*Annalen*, 1891, **265**, 354). The large excess of nitric acid, together with inadequate cooling, led to the formation of a dinitro-derivative, namely, *2-chloro-3 : 5-dinitroaceto-*p*-toluidide* (IX), which can readily be hydrolysed to the corresponding *amine* (X). The nitration of 2-chloroaceto-*p*-toluidide was then carried out after the method of Blanksma (*loc. cit.*), and the chloronitroacetotoluidide and the

corresponding amine obtained possessed the melting points recorded by Blanksma.

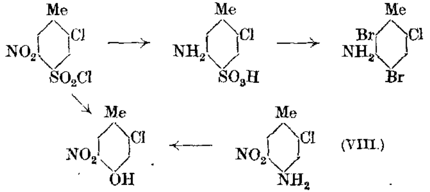


(IX.) (X.) (XI.)

The attempted transformation of the amine VIII into the corresponding phenol by means of the diazo-reaction at first gave negative results. Like many other diazo-compounds derived from halogen- or nitro-substituted amines (compare Cain, "The Diazo-compounds," 1920, 38), the diazo-compound produced in this case was very stable. It was found that the addition of the diazonium solution to boiling dilute sulphuric acid containing various amounts of sodium sulphate gave mere traces of a phenolic substance, but that when copper sulphate was present in the boiling acid mixture, the decomposition took the desired direction, and a 20 per cent. yield of the hydroxy-compound was obtained. It was shown by a mixed melting-point determination to be identical with the chloronitrocresol already obtained from the sodium chloronitrotoluenesulphonate.

It is therefore evident that the chloronitrotoluenesulphonyl chloride melting at 99·2° has the constitution indicated by II. The proof of the constitution of this substance is summarised as follows:

(II.)



(VIII.)

It was found later that a 5 per cent. yield of VIII was obtained by heating II under pressure with an alcoholic solution of ammonia.

The orientation of *2-chloro-6-nitro-p-toluenesulphonyl chloride* (III), m. p. 70°, was also unexpectedly difficult. Attempts to replace the sulphonyl chloride group by hydrogen were made under conditions similar to those already referred to (p. 853), but without success. It was similarly found impossible to replace the sulphonyl chloride group by chlorine, through the elimination of sulphur dioxide.

A consideration of the formula of 2-nitro-*p*-toluenesulphonyl chloride (XI) shows that all three groups will cause substitution to take place at the vacant ortho-position with respect to the methyl group. Chlorination of this substance would therefore be expected to lead to the formation of III. By a comparison of the chlorination product with the chloronitrotoluenesulphonyl chloride melting at 70°, it was hoped that the constitution of the latter substance would be established. 2-Chloro-*p*-toluenesulphonyl chloride was accordingly prepared (compare Reverdin and Crepieux, *Ber.*, 1901, **34**, 2992), and exposed to the action of chlorine at various temperatures (70—130°) in the presence of catalysts. Chlorination could not be effected.

In repeating a preparation of 2 : 6-dinitro-*p*-toluenesulphonic acid after Reverdin and Crepieux (*loc. cit.*), a by-product of about 2 per cent. of 2 : 4-dinitrotoluene was obtained, indicating that a sulpho-group may, when meta to a nitro-group, be replaced by another nitro-group. In order to convert the chloronitrotoluenesulphonyl chloride under investigation into a known chlorodinitrotoluene, it was heated with a nitrating mixture, but the sulpho-group was not eliminated, even under drastic conditions.

The constitution of the chloronitrotoluenesulphonyl chloride was finally elucidated by the action of sodium hydroxide solution. After prolonged boiling with the alkaline solution, acidification led to the production of no chloronitrocresol, which would probably have been formed had the chloronitrotoluenesulphonyl chloride had the constitution expressed by IV. On the other hand, when the cold acid solution was treated with sodium nitrite and poured into an alkaline solution of β-naphthol, a red dye was produced, indicating that an amino-derivative had been formed by the action of alkali on the chloronitrotolnenesulphonyl chloride. It is therefore very probable that auto-oxidation and reduction had taken place, with the production of a derivative of anthranilic acid, just as the action of alkali on 2-nitro-*p*-toluenesulphonic acid leads to the formation of *p*-sulphoanthranilic acid (D.R.-P. 138188). This reaction is only known to occur when the nitro- and methyl groups in nitrotoluene derivatives are in the ortho-position with respect to each other. There can therefore be little doubt that the chloronitrotoluenesulphonyl chloride melting at 70° has the formula III.

The chlorination of 2-chloro-*p*-toluenesulphonyl chloride was undertaken to ascertain whether the entering chlorine atom, like the nitro-group, would be directed chiefly into the 5-position. *p*-Toluenesulphonyl chloride has indeed been dichlorinated (D.R.-P. 210856), and the chlorinated product yielded, on the removal of the sulpho-group, a large proportion of 2 : 6-dichlorotoluene, with

some 2 : 3 : 6-trichlorotoluene. As the only evidence mentioned in favour of the dichlorotoluene being the 2 : 6-isomeride was the boiling point (190—200°), it was felt, in the light of the research already described, to be improbable that XII was the sole dichloro-*p*-toluenesulphonyl chloride produced.

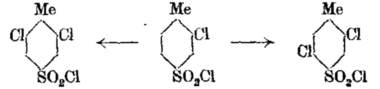
With antimony trichloride as catalyst, the chlorination of 2-chloro-*p*-toluenesulphonyl chloride took place smoothly at 65—70°. The patent seems to be practically justified, for the chief product was 2 : 6-dichloro-*p*-toluenesulphonyl chloride (XII). However, the presence of the expected isomeride (XIII) was shown.

The proportion of solid 2 : 6-dichloro-*p*-toluenesulphonyl chloride isolated was 66 per cent. of theory, and the amount actually formed must have been considerably greater, for it was not completely separated from the mixture of dichlorotoluenesulphonyl chlorides produced.

Sodium 2 : 6-dichloro-*p*-toluenesulphonate was hydrolysed very smoothly with the production of a dichlorotoluene which was converted into a dinitro-derivative melting at 121°. The dinitro-derivative of 2 : 6-dichlorotoluene melts at 121—122° (Cohen and Dakin, T., 1901, **79**, 1130). The dichlorotoluene was partly oxidised by nitric acid in a sealed tube and the acid produced shown to be identical with 2 : 6-dichlorobenzoic acid.

Advantage was taken of the steric hindrance to oxidation with permanganate solution, shown by 2 : 6-dichlorotoluene, in order to prove that 2 : 5-dichloro-*p*-toluenesulphonyl chloride (XIII) had been produced. The oil from which the solid 2 : 6-dichloro-*p*-toluenesulphonyl chloride had been separated was converted into the corresponding mixture of dichlorotoluenes, which was then oxidised by potassium permanganate solution. 2 : 5-Dichlorobenzoic acid was obtained. The proportion of 2 : 5-dichloro-*p*-toluenesulphonyl chloride was not determined, but it was small.

The results of the chlorination of 2-chloro-*p*-toluenesulphonyl chloride are represented in the diagram below.

(XII.)  (XIII.)

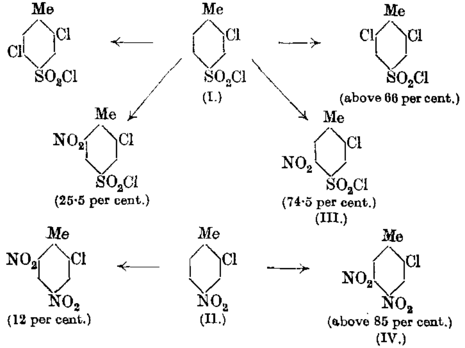
Chief product

Discussion of Results.

The nitration of I * shows that the *para*-directing influence of the chlorine atom is about three times as great as the combined *ortho*-

* The numbers used in the discussion refer to the formulæ on p. 859.

and meta-directing influences of the methyl and sulphonyl chloride groups respectively. An explanation of the apparently extraordinarily great influence of the chlorine atom can be deduced from a



consideration of the relative speeds of substitution caused by ortho-, para-, and meta-directing groups respectively. The order * in the two series is as follows:

$$OH > NH_2 > Cl > I > Br > CH_3$$
$$CO_2H > SO_3H > NO_2.$$

Hence it is very probable that the directing influence of the chlorine atom in I, weakened as it is by the presence of the methyl group in the ortho-position, is nevertheless of the same order as, and possibly greater than, the influence of the sulphonyl chloride group. This deduction can be tested by the results obtained in the nitration of II (compare Morgan and Drew, T., 1920, **117**, 786). The speed of substitution in the meta-position caused by the nitro-group is less than that caused by the sulpho-group (see above), and therefore presumably less than that caused by the sulphonyl chloride group. It would therefore be expected that the amount *of substitution in the para-position with respect to the chlorine atom* in I would be less than the amount of substitution in the same position in II. This expectation is borne out by the relative amounts of the nitro-derivatives actually formed.

* The order given in the two series is taken from Holleman's "Die direkte Einführung von Substituenten in den Benzolkern," 1910, 466, 469.

The results obtained show that in predicting the position chiefly taken up by a new fourth substituent, it is necessary to bear in mind the relative directing powers of the two positive * substituents. Even the difference in power of these two groups may be great enough to overwhelm the effect of the third, negative, group.

The foregoing remarks do not apply when the particular case of substitution is the entry of chlorine. It is, however, conceivable that when the directing influences of the substituents in the benzene nucleus more or less balance each other, the effect (usually quite secondary) of the nature of the entering group will then be much enhanced. This may be the reason why in I chlorination and nitration cause substitution to take place in different ways. This point is being studied with reference to other substances than I.

It is noteworthy that the sulphonyl chloride group in III and the nitro-group in the para-position to the chlorine atom (Morgan and Drew, *loc. cit.*) in IV are reactive towards ammonia and sodium hydroxide. This interesting and unexpected result may receive some explanation from the theory of Kenner (T., 1914, **105**, 2717; Kenner and Parkin, T., 1920, **117**, 852). This theory shows that the displacement of mobile substituents is presumably preceded by the formation of a molecular additive compound through the agency of the nitro-group in the ortho- or para-position with respect to the group which is actually displaced. The non-reactivity of the nitro-group in III indicates that the sulpho-group is incapable of forming such an additive compound.

Experimental.

2-Chloro-p-toluenesulphonyl Chloride.

The preparation, based on D.R.-P. 145908, was conducted a follows:

p-Toluenesulphonyl chloride (311 grams; 1 mol.) was melted wit antimony trichloride (6 grams), and chlorine introduced until th increase in weight was 57 grams (1 atom of chlorine). The chlori ation took place very smoothly, and the temperature was mai tained at 70—80° without external heating by adjusting the ra of flow of chlorine. The product, which solidified on cooling, w well stirred with water at 40°, extracted with warm benzene, t benzene solution filtered from antimony oxychloride, washed wi dilute sodium hydroxide solution, then with water, and dried ov

* The words "positive" and "negative" are used with the meani generally accepted in discussions on orientation, namely, ortho-para-, a meta-directing, respectively. It is often convenient (although really incorre ... all the halogens "positive" when describing their directive effect.

calcium chloride. The benzene was removed, and the sulphonyl chloride distilled under diminished pressure. A small amount of *p*-toluenesulphonyl chloride was obtained, b. p. 169°/38 mm., but the main fraction consisted of 276 grams of a colourless oil, b. p. 177—180°/38 mm. Finally, the dark residual liquid in the flask began to decompose, and was not examined.

The main fraction solidified on cooling, and melted at 32—36°. After redistillation it melted at 35—37°, and a portion crystallised from light petroleum in plates melting at 37—38°. The amide prepared from it melted at 137° after crystallisation from alcohol. Wynne and Bruce (T., 1898, **73**, 764) found the melting points of *2-chloro-p-toluenesulphonyl chloride and of the amide to be* 37° and 134° respectively.

2-Chloro-*p*-toluenesulphonyl chloride boils at 166°/24 mm. and 178°/36 mm., and its smell closely resembles that of *p*-toluenesulphonyl chloride.

*Nitration of 2-Chloro-*p*-toluenesulphonyl Chloride.*

2-Chloro-*p*-toluenesulphonyl chloride (100 grams) was gradually added with stirring to a cold mixture of nitric acid (50 c.c.; D 1·50) and sulphuric acid (125 c.c.), and the mixture stirred for two hours. The sulphonyl chloride at first liquefied, but when the nitration was complete it was converted into a solid of a butter-like consistence. The temperature was kept throughout at 20—30°. The product was poured into a large volume of cold water, and the heavy nitrated portion repeatedly stirred and pressed with cold water until free from acid. The pale yellow mass was allowed to remain overnight, *when it became quite hard and brittle. It was then powdered and* dried on a porous plate in a vacuum over calcium chloride. The yield was 109 grams and the melting point about 50—80°.

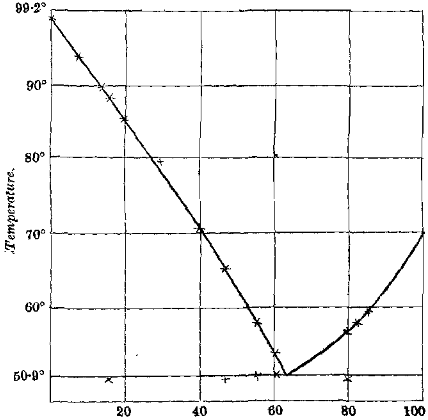
Slight hydrolysis of the sulphonyl chloride to the sulphonic acid occurred during nitration, but dinitro-derivatives were not produced even when ten times the amount of nitric acid theoretically required for mono-nitration were used.

Separation of the Isomerides.

A very convenient solvent for separating the isomerides formed was found to be light petroleum (b. p. 60—80°). After crystallising four times, most of the less soluble isomeride was obtained in prisms (60 grams), melting at 96—98°. The mother-liquor (500 c.c.) was concentrated to one-sixth of its volume, crystals and oil separated, and a further quantity of oil was formed on complete evaporation of the mother-liquor. The oil and crystals were mixed and

extracted with small portions of light petroleum (b. p. 40—60°) until half the mixture had gone into solution. The residue consisted almost entirely of the less fusible isomeride. The light petroleum solution slowly deposited long needles melting at 64—66°, together with some of the less fusible isomeride. By proceeding in this manner 12 grams of needles (m. p. 70°) and 80 grams of prisms (m. p. 99·2°) were obtained. The proportion of isomerides formed is, however, more accurately determined by the melting-point curve than by fractional crystallisation.

Melting-point curve of 2-chloro-5-nitro- and 2-chloro-6-nitro-p-toluenesulphonyl chlorides.



Percentage of 2-chloro-6-nitro-p-toluenesulphonyl chloride.

Proportion of the Isomerides formed in Nitration.

The melting-point curve of the two isomerides was obtained the usual way. When the less fusible isomeride was present i proportion greater than that required for the eutectic mixtu crystallisation took place very readily with only a small amo of supercooling, and the first-solidification points were obtai with a considerable degree of accuracy. But when the more fus isomeride was in excess of the eutectic mixture, crystallisation came extraordinarily sluggish. With slight supercooling crystall

tion took place so slowly that the thermometer in the mixture was scarcely affected, and even with considerable supercooling the solidification was extremely slow, although care was taken to have crystals of the more fusible isomeride on the sides of the tube. It is therefore probable that the first-solidification points obtained for the smaller branch of the curve are somewhat lower than they would have been had the crystallisation taken place with normal rapidity. This perhaps accounts for the fact that the shorter branch of the melting-point curve is slightly concave, as shown, whilst the longer branch is slightly convex. Slowness of crystallisation is not unknown in the case of mixtures of sulphonyl chlorides, especially when a large amount of the more fusible isomeride is present. For example, Holleman and Caland (*Ber.*, 1911, **44**, 2506), in finding the solidification points of mixtures of *o*- and *p*-toluenesulphonyl chlorides, give only one first-solidification point (but four second points), to determine the important portion of the curve corresponding with mixtures containing 60·4 to 100 per cent. of the more fusible isomeride.

It was fortunate that the portion of the curve required to determine the proportion of isomerides in the nitration product corresponds with mixtures, of which the first-solidification points were obtained without difficulty. It was therefore not thought necessary, for the purpose of this investigation, to determine the melting-point curve of the sulphonamides derived from the isomeric sulphonyl chlorides.

The solidification points obtained are as follows:

Percentage of the more fusible isomeride.	First-solidification point.	Second-solidification point.
0	99·2°	—
7·26	93·8	—
13·54	89·7	—
16·10	88·2	50·4°
19·54	85·2	—
28·94	79·6	—
39·50	70·6	—
46·98	65·2	50·5
55·40	58·0	50·8
60·72	54·0	50·9
79·68	56·6	50·5
82·10	58·0	50·8
85·41	59·2	—
100·00	70·0	—

The melting-point curve is constructed from these data. The eutectic mixture melts at 50·9° and contains 63·3 per cent. of the more fusible chloronitrotoluenesulphonyl chloride.

The nitration product (nitrated at 20—30° as described on p. 861) from pure 2-chlorotoluenesulphonyl chloride was washed free from

acid, powdered, and dried on a porous plate, and then allowed to remain under diminished pressure over phosphoric oxide.

The first- and second-solidification points were 81·5° and 49·8° respectively. Hence the nitration product was composed almost entirely of the two chloronitrotoluenesulphonyl chlorides isolated. Assuming the mixture to be a purely binary one, the proportion of the more fusible isomeride (2-chloro-6-nitro-*p*-toluenesulphonyl chloride) is therefore 25·5 per cent.

In order to ascertain whether a comparatively high temperature of nitration would considerably alter the proportion of isomerides formed, the nitration in the presence of sulphuric acid was carried out at 65—70°, with a slight excess of nitric acid; the weight of the product was 83·6 per cent. of theory. The two solidification points were 74·8° and 47—48° respectively. The second point was not at all sharp, but the solid nitration product softened at 47—48°. Fractional crystallisation of the mixture by means of light petroleum resulted in the separation of only the two chloronitrotoluenesulphonyl chlorides melting at 70° and 99·2°, the less fusible one predominating.

Owing to the fact that a considerable amount of hydrolysis of the sulphonyl chloride group had taken place during nitration, and since the second-solidification point showed that the mixture was not altogether a binary one, the relative amounts of the two isomerides can be determined only very approximately by means of the melting-point curve. The first point (74·8°) corresponds with 35 per cent. of the more fusible isomeride. The experiment is of interest when compared with the chlorination of 2-chloro-*p*-toluenesulphonyl chloride at 65—70° (see p. 871), because it shows that a comparatively high temperature is not the sole cause of substitution taking place in the ortho-position with respect to the methyl group.

*2-Chloro-5-nitro-*p*-toluenesulphonyl Chloride* (II, p. 853).

The above sulphonyl chloride crystallises from light petroleum in large, colourless prisms melting at 99·2°.* It is readily soluble in hot light petroleum (b. p. 60—120°), warm chloroform, col[d] ether, and benzene. It is only slightly soluble in cold light petro[le]um and in cold chloroform, and is much less soluble in these tw[o] solvents than the isomeride formed along with it (Found: N=5· $C_7H_5O_4NCl_2S$ requires N=5·2 per cent.).

* The melting points of all the new compounds described and of most the other substances prepared in this series of investigations were tak[en] with standardised, short, Anschütz thermometers.

The *amide* is prepared by the action of ammonia upon the sulphonyl chloride, and crystallises from water and from alcohol in small needles melting at 181° (Found: N=11·15. $C_7H_7O_4N_2ClS$ requires N=11·2 per cent.).

The *sulphonic acid* is formed by hydrolysing the sulphonyl chloride with concentrated hydrochloric acid in a sealed tube at 140—150°. It is moderately soluble in water, from which it crystallises in thick clusters of very small, non-deliquescent needles, and after drying at 120° melts at 123—128°.

The *sodium* salt, prepared by boiling the sulphonyl chloride with a slight excess of sodium hydroxide solution until the oil has disappeared (see p. 866), is very soluble in boiling water, moderately soluble in boiling alcohol (99 per cent.), and sparingly soluble in cold water and in cold alcohol. It crystallises from both solvents in very pale yellow needles, those from water containing two molecules of water of crystallisation. It can be obtained in colourless needles by neutralising the sulphonic acid. Both the sodium and barium salts are apt to decompose when heated above 220°, with the production of a black mass and of a vapour with a strong phenolic smell (Found: H_2O=11·7; Na=7·1. $C_7H_5O_5NClSNa,2H_2O$ requires H_2O=11·6; Na=7·4 per cent.).

The *barium* salt is formed by boiling the sulphonyl chloride with aqueous barium hydroxide. It is too soluble in water to be conveniently prepared from the sodium salt by double decomposition. The barium salt is almost insoluble in boiling alcohol (95 per cent.), and is very soluble in hot and moderately soluble in cold water, from which it separates in colourless scales containing two molecules of water of crystallisation (Found: H_2O=6·1; Ba=19·9. $(C_7H_5O_5NClS)_2Ba,2H_2O$ requires H_2O=5·35; Ba=20·4 per cent.).

6-*Chloro*-m-*toluidine*-4-*sulphonic Acid* (V, p. 854).

Anhydrous sodium 2-chloro-5-nitro-*p*-toluenesulphonate (5 grams), dissolved in a mixture of hot water (50 c.c.) and glacial acetic acid (25 c.c.), was treated gradually with iron filings (7 grams) and the flask heated, with frequent shaking, on the water-bath. After one hour the amino-acid began to separate from the hot solution. The reaction liquid was made alkaline with dilute sodium hydroxide solution, filtered while hot, and the cold filtrate acidified with hydrochloric acid. The amino-acid was rapidly precipitated, and a further qnantity was isolated by concentrating the mother-liquor. The total yield was 3·1 grams.

This *chlorotoluidinesulphonic acid* was only moderately soluble in boiling water, from which it was deposited on cooling in thin, small,

colourless, anhydrous plates, which readily turned red on exposure to light and air. The aqueous solution instantly decolorised bromine water, even in the cold (Found: in air-dried material, loss at 160°=0·4 per cent.; in dried acid, N=6·4. $C_7H_8O_3NClS$ requires N=6·3 per cent.).

*6-Chloro-2:4-dibromo-*m*-toluidine* (VI, p. 854).

The preceding chlorotoluidinesulphonic acid (1 gram) was dissolved in boiling water (50 c.c.), bromine water was added until it was no longer decolorised, and the flocculent precipitate produced was collected after remaining overnight. The filtrate contained sulphuric acid. The precipitate (1 gram) was crystallised from boiling alcohol.

*6-Chloro-2:4-dibromo-*m*-toluidine* is readily soluble in boiling alcohol and slightly soluble in cold alcohol, from which it crystallises in long, colourless needles melting at 99·5°, which, on keeping, become light red. It does not dissolve in dilute hydrochloric acid, and is slightly soluble in hot fuming hydrochloric acid [0·1214 gave 0·2079 (AgCl+AgBr); theo. for $C_7H_6NClBr_2$, 0·2106].

*2-Chloro-5-nitro-*p*-cresol* (VII, p. 855).

In the preparation of sodium 2-chloro-5-nitro-*p*-toluenesulphonate it was noticed that the alkaline solution became red and that the red colour disappeared on acidification. When the strongly alkaline solution was boiled for several hours a red, insoluble substance was formed, and very violent "bumping" ensued. This inconvenience was largely obviated when the hydrolysis was effected with dilute sodium hydroxide solution in the following way.

A mixture of the sulphonyl chloride (27 grams; 1 mol.) and *N*-sodium hydroxide (600 c.c.; 50 per cent. in excess of the 4 mols. theoretically required) was boiled under reflux for seventy-two hours, a glistening, red precipitate being gradually deposited. The red liquid was acidified by hydrochloric acid and the brown solution distilled in a current of steam. The pale yellow substance that solidified in the condenser melted without further purification at 70°. The yield was 4·1 grams or 22 per cent. of theory. The hydrolysis may be advantageously effected by potassium hydroxide solution, the potassium salt of the chloronitrocresol being so soluble that risk of "bumping" is eliminated.

When pure sodium chloronitrotoluenesulphonate was heated with sodium hydroxide solution, only a small amount of sodium chloride was produced. There was no appreciable quantity of

sodium nitrite formed even after boiling for seventy-two hours, for nitrous fumes were not produced on acidification.

2-*Chloro-5-nitro*-p-*cresol* sublimes in long, thin, lemon-coloured needles melting at 71°. It is very volatile with steam, and has a faint odour, much more pronounced in the hot, which recalls the tarry smell of *o*-nitrophenol. It is very soluble in cold ether, alcohol, acetone, or benzene, moderately soluble in cold chloroform, ethyl acetate, glacial acetic acid, or light petroleum (b. p. 60—80°), slightly soluble in hot water and sparingly soluble in cold water. It crystallises from all these solvents in long, yellow needles. The alkali salts are very intensely coloured. A colourless aqueous solution of the chloronitrocresol (1 : 100,000) becomes yellow on the addition of sodium hydroxide solution, and colourless again on acidification (Found: N=7·41; Cl=19·0. $C_7H_6O_3NCl$ requires N=7·46; Cl=18·9 per cent.).

The *benzoyl* derivative, prepared in the usual way, is easily hydrolysed by sodium hydroxide, and crystallises from alcohol in colourless needles melting at 129° (Found: C=57·4; H=3·55. $C_{14}H_{10}O_4NCl$ requires C=57·6; H=3·4 per cent.).

The alkali salts of the chloronitrocresol are of interest on account of their great difference in solubility.

The *sodium* salt, prepared by adding the finely powdered chloronitrocresol to a boiling, dilute solution of sodium hydroxide, and filtering when cold, is a red powder, amorphous when viewed under the microscope (Found: Na=10·8. $C_7H_5O_3NClNa$ requires Na=11·0 per cent.). It is very sparingly soluble in cold water, and slightly soluble in boiling water. The latter reagent slowly effects hydrolysis, chloronitrocresol volatilising in the steam. The sodium salt rapidly separates when a 5 per cent. solution of sodium sulphate is mixed with a cold, moderately concentrated solution of the potassium salt of the chloronitrocresol.

The *lithium* salt is also very slightly soluble in water, and is obtained from the potassium salt as an orange-red, amorphous powder.

The *potassium* salt, prepared by the action of potassium hydroxide solution on the chloronitrocresol, is very soluble in boiling water and moderately soluble in cold water, from which it separates in magnificent, long, anhydrous, crimson needles. When heated at 170°, the crystals become almost black, but regain their original colour on cooling (Found: in air-dried material, loss at 170°=0·9 per cent. In anhydrous material, K=17·1. $C_7H_5O_3NClK$ requires K=17·3 per cent.).

The *ammonium* salt is very soluble in hot dilute ammonia, from which it slowly separates on cooling in long, orange-red needles,

t is very easily hydrolysed, ammonia being lost by mere exposure o the air.

The rubidium and cæsium salts of the chloronitrocresol are not precipitated when aqueous solutions of any rubidium and cæsium alts are separately added to a solution of the potassium salt.

*Synthesis of 2-Chloro-5-nitro-*p*-cresol* (VII, p. 855).

2-Chloro-*p*-nitrotoluene (b. p. 260°/760 mm.; m. p. 63—65°), prepared by the chlorination of *p*-nitrotoluene at 60—70° in the presence of a small amount of antimony trichloride, was reduced almost quantitatively with iron filings and hydrochloric acid to 2-chloro-*p*-toluidine (m. p. 26°; b. p. 242—244°/760 mm. Lellmann, *Ber.*, 1884, **17**, 535, gives 26° and 237—238·5° respectively). This toluidine was acetylated, and the properties of the chloroacetotoluidide agreed with those described by Knuckell and Lillig (*J. pr. Chem.*, 1912, [ii], **86**, 715). They, however, incorrectly state that this chloroacetotoluidide is insoluble in water; it is slightly soluble in boiling water, from which it crystallises on cooling in needles about 3 cm. long.

The preparation of 2-chloro-5-nitro-*p*-toluidine (VIII, p. 855) by Claus and Bocher's method (*loc. cit.*) was attempted by gradually adding 2-chloroaceto-*p*-toluidide (10 grams) to well-cooled nitric acid (D=1·5; 40 c.c.) and after an interval of six hours pouring the dark red solution into water. The orange powder obtained was crystallised from alcohol, when *2-chloro-3 : 5-dinitroaceto-*p*-toluidide* (IX, p. 855) separated in colourless leaflets, m. p. 238° (Found: N=15·3. $C_9H_8O_5N_3Cl$ requires N=15·4 per cent.). It was hydrolysed by stirring with cold sulphuric acid until a clear solution was formed, and after five minutes pouring the mixture into cold water, when a yellow precipitate was immediately produced, from which by crystallisation from alcohol *2-chloro-3 : 5-dinitro-*p*-toluidine* (X, p. 855) was obtained in thin, golden-yellow needles melting at 137° (Found: N=18·3. $C_7H_6O_4N_3Cl$ requires N=18·1 per cent.). The alcoholic solution has an extremely pleasant, fruity smell. Both the amine and its acetyl derivative are only very slightly soluble in cold water. The amine dissolves with difficulty in cold concentrated hydrochloric acid, and is immediately precipitated on dilution.

Since 2-chloro-5-nitroaceto-*p*-toluidide had not been produced by the preceding method, the nitration of *o*-chloroaceto-*p*-toluidide was carried out after the method of Blanksma (*loc. cit.*). A comparatively small excess of nitric acid was used, the time of reaction was not prolonged, the temperature was kept below 15° during the nitration, and the liquid was finally poured on crushed ice. In

this way the chloronitroacetotoluidide required was obtained in good yield in pale yellow needles melting at 112°. Hydrolysis and simultaneous crystallisation of the amine were conveniently carried out by mixing the chloronitroacetotoluidide, dissolved in as little boiling alcohol as possible, with a slight excess of boiling 40 per cent. sodium hydroxide solution, when hydrolysis instantly took place and the amine rapidly separated in leaflets, m. p. 165°.

*Conversion of 2-Chloro-5-nitro-*p*-toluidine into 2-Chloro-5-nitro-*p*-cresol.*—A solution of the foregoing chloronitrotoluidine (5 grams) in a mixture of concentrated sulphuric acid (15 c.c.) and water (5 c.c.) cooled to 10°, was diazotised with sodium nitrite (3 grams) in water (10 c.c.), the temperature throughout being kept below 20°. The filtered diazonium solution was slowly added to a boiling mixture (b. p. about 116°) of 20 grams of crystallised copper sulphate, 45 grams of anhydrous sodium sulphate, 30 c.c. of concentrated sulphuric acid, and 100 c.c. of water. The phenol, being very volatile with steam, was driven over almost as fast as it was formed; the last traces were removed with the aid of steam. The oil in the distillate, which refused to solidify, was made alkaline with sodium hydroxide, the red sodium salt produced (1·2 grams), having been washed with water, alcohol, aud ether, was acidified, and the phenol distilled with steam. It melted at 50—60°, and crystallised from alcohol, ether, benzene, or light petroleum in long, yellow needles, which did not, however, melt sharply, and even after sublimation the melting point was 57—63°. The substance was finally purified by conversion into the benzoyl derivative, which crystallised from alcohol in colourless needles, m. p. 129°. The benzoyl compound was hydrolysed by boiling for five minutes with a methyl-alcoholic solution of sodium hydroxide, tbe red salt filtered, washed with water and alcohol, acidified, and the phenol extracted with ether. It crystallised in long, yellow needles, which melted at 70°, and after sublimation at 71°. The 2-chloro-5-nitro-*p*-cresol obtained in this way was identified by the method of mixed melting-point with the chloronitrocresol obtained from the less fusible chloronitrotoluenesulphonyl chloride, the constitutions VII (p. 855) and II (p. 853) respectively of these two compounds being thereby established.

It was afterwards found that the sodium salt of the chloronitrotoluenesulphonic acid could be made to yield a small quantity of 2-chloro-5-nitro-*p*-toluidine as follows:

The anhydrous, finely powdered sodium salt (2 grams) was covered with 10 c.c. of 10 per cent. aqueous ammonia (about four times the theoretical amount) and heated in a sealed tube for thirty-six hours at 135—145°. A yellow solution was formed, which

deposited some unchanged sodium salt in needles. The ammonia was driven off and a current of steam passed through the residue, when a small quantity of a yellow solid distilled. The yellow distillate was extracted with ether, the ethereal solution dried over solid sodium hydroxide, the ether removed, and the yellow residue dissolved in alcohol, from which 2-chloro-5-nitro-*p*-toluidine separated in orange leaflets melting at 165° (yield 0·03 gram). It was identified by a mixed melting-point determination with the chloronitro-*p*-toluidine (m. p. 165°) prepared above.

A 5 per cent. yield was obtained by using, under the same conditions, alcoholic instead of aqueous ammonia. In neither case was ammonium (or sodium) chloride formed, and nitrite was shown to be absent by acidifying in the cold and pouring the solution into an alkaline solution of β-naphthol, when no red coloration was produced.

*2-Chloro-6-nitro-*p*-toluenesulphonyl Chloride* (III, p. 853).

This compound is far more soluble in chloroform or light petrol eum than the isomeride already described, and it is extremel soluble in ether or benzene. The best crystallising medium i light petroleum (b. p. 40—60°), from which it separates in lon colourless needles melting at 70° (Found: N=5·1. $C_7H_5O_4NCl_2$ requires N=5·2 per cent.).

The *amide* crystallises from water in shining scales, and slow from alcohol in needles. Both forms melt at 182° (Found: N=11· $C_7H_7O_4N_2ClS$ requires N=11·2 per cent.).

The *sulphonic acid*, prepared by hydrolysis of the sulphon chloride with concentrated hydrochloric acid in a sealed tube 165—185°, was obtained free from hydrochloric acid by addi water and evaporating almost to dryness on the water-bath, th process being repeated several times. In this way the acid w isolated in deliquescent plates very soluble in water.

The *sodium* salt was obtained by heating the chloronitrosulpho chloride (5 grams) with 5 per cent. sodium hydroxide soluti (40 c.c.) on the water-bath until the oily sulphonyl chloride h disappeared. The solution was then neutralised by hydrochlo acid and concentrated, and the *sodium* salt which separated cooling crystallised from water until free from sodium chloride.

The *sodium* salt forms colourless, anhydrous, microscopic pla which are not altered by heating at 180°. It is far more solubl cold water than the sodium salt of the isomeride (p. 865), an almost insoluble in boiling 99 per cent. alcohol (Found: Na= $C_7H_5O_5NClSNa$ requires Na=8·4 per cent.).

The *potassium* salt rapidly separates in colourless laminæ when dilute solutions of the sodium salt and potassium sulphate are mixed.

The *barium* salt is formed by adding barium chloride solution to a concentrated aqueous solution of the sodium salt. It separates from cold water in colourless leaflets containing three molecules of water of crystallisation. It is readily soluble in boiling alcohol, from which it separates on cooling in glistening laminæ (Found: $H_2O=8{\cdot}1$. $(C_7H_5O_5NClS)_2Ba,3H_2O$ requires $H_2O=7{\cdot}8$ per cent. Found: in anhydrous salt, $Ba=21{\cdot}25$. $(C_7H_5O_5NClS)_2Ba$ requires $Ba=21{\cdot}5$ per cent.).

The *constitution* of the *chloronitrotoluenesulphonyl chloride* was determined by the action of sodium hydroxide solution on the sodium salt of the acid.

The sodium salt (2 grams) was boiled for eight hours with 10 per cent. sodium hydroxide solution (20 c.c.). The solution rapidly became brown and very slightly turbid. Excess of hydrochloric acid was added and a portion of the solution, still brown, distilled in a current of steam. There was no evolution of sulphur dioxide and no organic substance distilled. The other portion of the solution did not yield any organic substance to ether.

Some of the acid solution was diluted until it was almost colourless, cooled, and after the addition of sodium nitrite poured into an alkaline solution of β-naphthol, when a deep red coloration was at once formed and a small quantity of red powder slowly separated.

Owing to the small amount of sodium chloronitrotoluenesulphonate available it was not possible to obtain the chloroaminosulphobenzoic acid in a pure state. It was found, however, that an amino-derivative was formed when the sodium chloronitrotoluenesulphonate was boiled for five minutes with 20 per cent. sodium hydroxide solution.

This experiment shows that the formula (III) assigned to the more fusible chloronitrotoluenesulphonyl chloride is correct.

*The Action of Chlorine on 2-Chloro-*p*-toluenesulphonyl Chloride.*

2 : 6-*Dichloro-*p*-toluenesulphonyl Chloride* (XII, p. 858).—A fused mixture of 2-chloro-*p*-toluenesulphonyl chloride (125 grams) and antimony chloride (5 grams) was chlorinated at 65—70° for two hours until the necessary increase in weight (19·2 grams) was attained. The chlorinated product partly crystallised after remaining overnight in a desiccator. The crystals were collected and after drying on a porous plate weighed 68 grams and melted at 58—62°. The oily filtrate was purified from antimony chloride by pouring into water, extracting with benzene, and washing the

benzene solution with alkali and with water. After the extract had been dried with calcium chloride, the benzene was completely removed and the residual oil (71 grams) distilled in a vacuum. The first fraction, b. p. 168—178°/28 mm. (10 grams), consisted largely of unchanged chlorotoluenesulphonyl chloride. The second fraction (30 grams), b. p. 178—185°/28 mm., and the third fraction (23 grams), b. p. 185—195°/28 mm., were chiefly composed of dichloro-*p*-toluenesulphonyl chlorides. The three fractions were kept at 0° for several hours, and the crystals produced from each fraction in order of ascending boiling point weighed, after drying on porous plate at the ordinary temperature, 3, 10, and 18 grams respectively. The crystals melted at about 57—61° and were purified by crystallisation from light petroleum. The total yield of 2 : 6-dichloro-*p*-toluenesulphonyl chloride melting at 66—68° was 95 grams or 66 per cent. of the theoretical yield.

2 : 6-*Dichloro*-p-*toluenesulphonyl chloride* separates very slowly from cold light petroleum (b. p. 80—100°) in plates melting at 66—68°. Several recrystallisations are required to produce the pure substance in large, flat plates melting at 69°. The chief impurity, m. p. 218°, crystallises in fine, hair-like, colourless needles, is only slightly soluble in cold organic solvents, and appears to be pentachlorotoluene. The sulphonyl chloride is extremely soluble in cold benzene or ether, and moderately soluble in cold light petroleum (Found: Cl=40·2. $C_7H_5O_2Cl_3S$ requires Cl=41·0 per cent.).

It is very slowly oxidised by fuming nitric acid in a sealed tube at 230°.

The *sulphonic acid*, prepared from the barium salt in the usual way, crystallises in colourless, deliquescent plates and is very soluble in water.

The *amide* is slightly soluble in hot water, from which it separates in shining scales melting at 191° (Found: N=5·8. $C_7H_7O_2NCl$ requires N=5·8 per cent.).

The *sodium* salt crystallises from water in clusters of fan-like divergent, colourless needles, slightly soluble in cold, readily soluble in hot water. The crystals contain one molecule of water (Found: H_2O=6·8; Na=8·2. $C_7H_5O_3Cl_2SNa,H_2O$ requires H_2O=6·4; Na= 8·2 per cent.).

The *barium* salt is formed from a solution of the sodium salt by precipitation with barium chloride. It dissolves sparingly in cold water and is moderately soluble in hot water, from which it crystallises in thin, minute, silky needles containing three molecules of water of crystallisation (Found: loss at 180°=8·2. $C_{14}H_{10}O_6Cl_4S_2Ba,3H_2O$ requires H_2O=8·05 per cent. Found: in anhydrous material Ba=22·7. $C_{14}H_{10}O_6Cl_4S_2Ba$ requires Ba=22·3 per cent.).

Conversion of the Dichlorotoluenesulphonic Acid into 2 : 6-Dichlorotoluene.

Hydrolysis occurred very readily when a solution of the hydrated sodium salt (9 grams) in water (15 c.c.) and sulphuric acid (50 c.c.) was distilled in superheated steam at 250°. The oil was extracted from the distillate with chloroform, the solution dried with solid sodium hydroxide, the chloroform removed, and the oil distilled, when it passed over almost completely at 197—199°/757 mm., and weighed 3·5 grams.

The dinitro-derivative of the dichlorotoluene was prepared in the usual way and melted at 121° (Cohen and Dakin, T., 1901, **79**, 1132, give m. p. 121—122°) (Found: N=11·0. Calc., N=11·15 per cent.).

The dichlorotoluene obtained by the hydrolysis of the dichloro-*p*-toluenesulphonic acid was finally converted into 2 : 6-dichlorobenzoic acid, a process which presented some difficulty.

The dichlorotoluene was boiled for twelve hours with a slight excess of dilute aqueous potassium permanganate solution, whereby only a trace of the dichlorotoluene was attacked. It was impossible to detect any dichlorobenzoic acid, even when the aqueous solution was concentrated to a very small volume before decolorising by sulphur dioxide. It was similarly found impossihle to prepare a dichlorobenzoic acid by oxidising the dichlorotoluene with potassium permanganate in acetone solution.

Cohen and Dakin (*loc. cit.*) partly oxidised 2 : 6-dichlorotoluene by heating with nitric acid in a sealed tube. The dichlorotoluene (2 grams) under investigation was accordingly heated with nitric acid (15 c.c.; D=1·2) in a sealed tube for a week. The oil produced partly solidified when cooled. The solid (0·5 gram) was collected, and treated with sodium carbonate solution, in which it only partly dissolved. The acid which was precipitated from the acidified filtrate crystallised from light petroleum (b. p. 80—100°) in needles melting at 136—138°. Repeated recrystallisation from different solvents failed to raise the melting point above 137—139°. Mixtures of these crystals with 2 : 6-dichlorobenzoic acid (m. p. 144°) * and with 2 : 5-dichlorobenzoic acid (m. p. 154°) melted at 137—140° and below 120° respectively.

* Holleman and Bornwater (*Rec. trav. chim.*, 1912, **31**, 221) show how the melting points assigned to 2 : 6-dichlorobenzoic acid vary from 126·5° to 143·7°. A pure product is formed by the oxidation of 2 : 6-dichlorobenzaldehyde by potassium permanganate in acetone solution. I am greatly indebted to Mr. G. R. Clemo for pure specimens of 2 : 6- and 2 : 5-dichlorobenzoic acids.

The solid oxidation product that was insoluble in sodium carbonate solution crystallised from alcohol in colourless needles melting at 68°. It was shown not to be 2 : 6-dichlorobenzaldehyde (*mixed melting point*), and cannot be 2 : 6-dichloro-3-nitrobenzaldehyde, which consists of colourless plates melting at 76—77° (D.R.-P. 199943). There was not enough of the substance for further examination.

These experiments clearly show that the dichlorotoluene in question is 2 : 6-dichlorotoluene, and that the dichlorotoluenesulphonyl chloride described has the formula XII.

*The Formation of 2 : 5-Dichloro-*p*-toluenesulphonyl Chloride in the Chlorination of 2-Chloro-*p*-toluenesulphonyl Chloride.*

The liquid portion of the fraction, b. p. 178—185°/28 mm. (p. 872), from which 2 : 6-dichloro-*p*-toluenesulphonyl chloride was separated, was boiled with excess of sodium hydroxide solution, and after cooling the precipitated sodium salts were collected. Hydrolysis was effected by dissolving the mixed sodium salts (10 grams) in a mixture of sulphuric acid (35 c.c.) and water (10 c.c.), and passing superheated steam at 250°. An oil (4 grams) was produced, which after being extracted with chloroform and dried with sodium hydroxide boiled at 160—200°, mostly at 180—200°. One gram of the fraction boiling at 180—200° (which must be free from any *o*-chlorotoluene, b. p. 160°) was boiled for ten hours with 2 grams of potassium permanganate dissolved in 200 c.c. of water. The oil was not completely oxidised, although the solution was still red. The solution was concentrated to 30 c.c. and treated with sulphur dioxide, whereby 0·3 gram of an acid was precipitated, which on crystallising from light petroleum (b. p. 60—80°) formed colourless needles melting at 136—142°. Recrystallisation failed to raise the melting point. A mixture with 2 : 5-dichlorobenzoic acid (m. p. 154°) melted at 136—142°, mostly 142°. Hence the acid melting at 136—142° was somewhat impure 2 : 5-dichlorobenzoic acid. It follows that a mixture of 2 : 6- and 2 : 5-dichloro-*p*-toluenesulphonyl chlorides is produced when 2-chloro-*p*-toluenesulphonyl chloride is chlorinated.

Summary.

(I) The nitration of 2-chloro-*p*-toluenesulphonyl chloride in mixed nitric and sulphuric acids at 20—30° leads to the formation of a mixture of isomeric mononitro-derivatives (more than 90 per cent. of the theoretical amount). The nitration product consists of

2-chloro-5-nitro-*p*-toluenesulphonyl chloride and 2-chloro-6-nitro-*p*-toluenesulphonyl chloride almost exactly in the proportion of three to one.

(II) The proportion of the two isomerides shows that the orientation due to the chlorine atom is much greater under these conditions than the united directive effects of the methyl and sulphonyl chloride groups. The proportion of isomerides is not greatly altered by nitration at 65—70°.

(III) The sulphonyl chloride group and not the nitro-group in *2-chloro-5-nitro-p-toluenesulphonyl chloride* is somewhat reactive, and can be replaced by a hydroxy-group by boiling with dilute alkali hydroxide solution.

(IV) Monochlorination of 2-chloro-*p*-toluenesulphonyl chloride at 65—70° results in a mixture of isomerides, 2 : 6-dichloro-*p*-toluenesulphonyl chloride being the chief product (upwards of 66 per cent.). 2 : 5-Dichloro-*p*-toluenesulphonyl chloride is also formed.

(V) Hence the nature of the group entering the benzene nucleus in 2-chloro-*p*-toluenesulphonyl chloride may be an important factor in deciding the position of the substituent.

The author desires to express his thanks to Professor W. H. Perkin and to Dr. E. Hope for suggesting this research and for their advice. His thanks are also due to Mr. Fred Hall for assistance in the nitrogen, carbon, and hydrogen estimations, and to the Advisory Council for Scientific and Industrial Research for a grant which has partly defrayed the expenses of the first portion of this investigation. The author also wishes to make acknowledgment to the Ramsay Memorial Fellowship Trust for a Fellowship which has enabled this portion of the research to be completed.

The Dyson Perrins Laboratory,
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[*Received, March 30th*, 1921.]

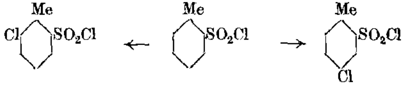
XCVII.—*The Cumulative Effect of the Chlorine Atom and the Methyl and Sulphonyl Chloride Groups on Substitution in the Benzene Nucleus. Part II.*

By WILLIAM DAVIES.

IT has been shown in the previous communication, by the nitration of 6-chloro-*p*-toluenesulphonyl chloride, that the para-directing influence of the chlorine atom is greater than that of the sulphonyl chloride group, together with the ortho-directing influence of the methyl group. In order to determine whether the combined para- and meta-directing influences of the methyl and sulphonyl chloride groups would similarly be overpowered, the nitration of 6-chloro-*o*-toluenesulphonyl chloride was studied.

6-Chloro-*o*-toluenesulphonyl chloride (I) was isolated in nearly 40 per cent. yield from the product of chlorination of *o*-toluenesulphonyl chloride. Its constitution was shown by converting it into *o*-chlorobenzoic acid. The other isomeride formed—doubtless 4-chloro-*o*-toluenesulphonyl chloride (II)—boils at the same temperature, and a complete method of separation has not yet been devised.

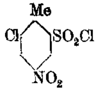
6-*Chloro*-o-*toluenesulphonyl chloride* (m. p. 71—72°) was converted into the corresponding *sulphonic acid* and the characteristic *sodium* and *barium* salts. The *amide* (m. p. 180°) was transformed by gentle oxidation into "*6-chlorosaccharin*" (m. p. 210—212°), which is more than half as sweet as "saccharin," but has a somewhat astringent taste.



(I.) (II.)

The nitration of 6-chloro-*o*-toluenesulphonyl chloride at 20—30° leads to the formation of a mixture of 6-chloro-3-nitro-*o*-toluenesulphonyl chloride (III) and 6-chloro-4-nitro-*o*-toluenesulphonyl chloride (IV) in the proportion of 40 and 60 per cent. respectively. The two substances can be partly separated by means of light petroleum, in which III is slightly less soluble than IV. A thorough separation is effected by means of the barium salts of the corresponding acids, that derived from III being extremely soluble in alcohol.

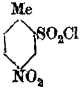
(V.) (III.)



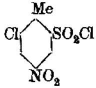
(IV.)

6-Chloro-3-nitro-*o*-toluenesulphonyl chloride (III) could not be converted into a chloronitrotoluene by hydrolysis of the sulphonyl chloride group. It was, however, transformed into the sodium salt of a chloronitrocresol by boiling with sodium hydroxide solution. The chloronitrocresol, which could not be benzoylated, had the properties of an o-nitrophenol and melted at 64°. It was shown to be identical with 6-chloro-3-nitro-*o*-cresol (V), a specimen of which was prepared from 6-chloro-*o*-nitrotoluene in the manner described by Noelting (*Ber.*, 1904, **37**, 1015). The 6-chloro-*o*-nitrotoluene required was obtained in 24·7 per cent. yield by the chlorination of *o*-nitrotoluene at 55—60° in the presence of a small proportion of antimony trichloride (compare Jansen, D.R.-P. 107505).

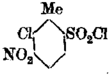
The constitution of 6-chloro-4-nitro-o-toluenesulphonyl chloride (IV) was shown by its behaviour towards boiling sodium hydroxide solution. A dark red solution was rapidly formed and the coloration was not destroyed by acidification, but on the contrary the solution stained the skin dark yellow. For purposes of comparison, 4-nitro-o-toluenesulphonyl chloride (VI) was boiled with sodium hydroxide solution and similar colorations were produced. It is therefore very probable that the dyes formed by the action of alkali on the chloronitrotoluenesulphonyl chloride are of the same type as those formed by the same treatment of 4-nitro-o-toluenesulphonyl chloride. The latter dyes, however, are stilbene derivatives (compare Cain and Thorpe, "The Synthetic Dyestuffs," p. 48), which are never formed by the action of alkalis on derivatives of *m*-nitrotoluene. Hence the chloronitrotoluenesulphonyl chloride under investigation cannot have the formula VII, and must therefore have that indicated by IV.



(VI.)



(IV.)



(VII.)

This research shows that the chlorine atom in 6-chloro-*o*-toluenesulphonyl chloride has a slightly smaller orientating effect than the other two groups acting together, as far as substitution by the

nitro-group is concerned. It is interesting to note that the chlorine atom in 2-chloro-6-nitrotoluene has, under somewhat similar conditions (Morgan and Jones, this vol., p. 187), an almost overwhelming directive influence. It follows that the sulphonyl chloride group has a more powerful orientating effect than the nitro-group.

EXPERIMENTAL.

Purification of o-*Toluenesulphonyl Chloride.*

o-Toluenesulphonyl chloride, kindly supplied by Messrs. Boots, Ltd., was obtained almost completely pure by distillation in a vacuum after the method of Ullmann and Lehner (*Ber.*, 1905, **38**, 730). It was found advisable to distil under somewhat greater pressure than they used, the difference in boiling points of the ortho- and para-isomerides thus being increased, and the decomposition that ensued being quite negligible. In this way the first fraction finally obtained gave an amide melting at 155°. As *o*-toluenesulphonamide melts at 156·3° (McKie, T., 1918, **113**, 801), the *o*-toluenesulphonyl chloride had evidently been obtained in an almost pure state.

The ortho-isomeride boils at 151°/33 mm. and 154°/36 mm., and the para-isomeride at 164°/33 mm. and 167°/36 mm.

6-Chloro-o-toluenesulphonyl Chloride.

6-Chloro-*o*-toluenesulphonyl chloride was first made by chlorinating *o*-toluenesulphonyl chloride in the presence of antimony trichloride and working up the product as described in the preparation of 2-chloro-*p*-toluenesulphonyl chloride (this vol., p. 860). The mixture of monochloro-*o*-toluenesulphonyl chlorides produced boiled at 165—169°/33 mm., and about 41 per cent. of this liquid solidified on cooling. The solid portion consisted of the desired isomeride in an almost pure state.

A considerable improvement in the method of preparation was effected by using only a small amount of the catalyst. Chlorination so rapid that the temperature (75—90°) was maintained without external heating could be brought about (with anhydrous materials) when the weight of the antimony trichloride was 1 per cent. of the weight of *o*-toluenesulphonyl chloride. With no catalyst present, however, a reaction did not take place at all readily. In this way, by allowing the pale yellow chlorinated product to remain in a freezing mixture, the 6-chlorotoluenesulphonyl chloride separated out, and by filtering at the ordinary temperature (in order to prevent the separation of a eutectic mixture of the isomerides),

it was obtained in greater yield than by the tedious process indicated above.

The chlorinated product (740 grams containing 40 grams of antimony trichloride) gave 270 grams of dry 6-chloro-*o*-toluenesulphonyl chloride, the yield being 38·6 per cent. of the theoretical. The product was almost pure, and after one crystallisation from light petroleum (b. p. 80—100°) melted at 69—70°. It is noteworthy that the yield is materially decreased by using *o*-toluenesulphonyl chloride not completely freed from *p*-toluenesulphonyl chloride.

*6-Chloro-*o*-toluenesulphonyl chloride* crystallises in large, thick, white prisms closely resembling potassium iodide in appearance, and the smell recalls that of *o*-toluenesulphonyl chloride, but is comparatively faint. The substance is very soluble in cold benzene, much less so in cold light petroleum, and is obtained by recrystallisation from light petroleum (b. p. 60—80°) in plates softening at 71° and melting at 72°. It is very slowly oxidised by fuming nitric acid in a sealed tube at 230° (Found: Cl=31·0. $C_7H_6O_2Cl_2S$ requires Cl=31·55 per cent.).

The constitution of this chlorotoluenesulphonyl chloride was shown by converting it into *o*-chlorobenzoic acid. The sulphonyl chloride (15 grams) was gently boiled under reflux with a mixture of sulphuric acid (40 c.c.) and water (10 c.c.), and when the oil had disappeared, steam at 150° was passed through the dark red solution until the distillate was no longer cloudy. The oil (5 grams) was extracted with chloroform, dried with calcium chloride, the chloroform removed, and the oil distilled. It boiled almost entirely at 150—160°. The oil (2 grams) was boiled for five hours with potassium permanganate (5 grams) dissolved in water (300 c.c.), and the solution was concentrated and then treated with sulphur dioxide until it became colourless. Long, colourless needles slowly separated, which after drying on a porous plate melted at 140°. The melting point was unchanged by admixture of *o*-chlorobenzoic acid, m. p. 140°.

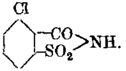
*6-Chloro-*o*-toluenesulphonic acid*, prepared from the barium salt in the usual way, forms thin, lustrous, non-deliquescent laminæ. It is readily soluble in cold water, melts at 60—70°, and when anhydrous melts at about 72° (Found: in anhydrous material, C=40·5; H=3·5. $C_7H_7O_3ClS$ requires C=40·7; H=3·4 per cent.).

The *amide* crystallises in glistening scales from hot water, in which it is moderately soluble. It melts at 180° and tastes slightly bitter (Found: N=6·7. $C_7H_8O_2NClS$ requires N=6·8 per cent.).

The *sodium* salt is formed by hydrolysing the sulphonyl chloride with sodium hydroxide solution. It is slightly soluble in boiling

alcohol, readily soluble in hot, and slightly soluble in cold water, from which it separates in large, glistening laminæ containing one molecule of water of crystallisation (Found: $H_2O=7{\cdot}6$; $Na=9{\cdot}0$. $C_7H_6O_3ClSNa,H_2O$ requires $H_2O=7{\cdot}3$; $Na=9{\cdot}3$ per cent.).

. The *barium* salt is conveniently made by adding dilute barium chloride solution to a hot solution of the sodium salt, when the barium salt is rapidly precipitated. It is almost insoluble in boiling alcohol, slightly soluble in boiling, and sparingly soluble in cold water, from which it crystallises in small, lustrous flakes containing one molecule of water of crystallisation (Found: loss at 180° = 3·1; Ba = 24·1. $[C_7H_6O_3ClS]_2Ba,H_2O$ requires $H_2O=3{\cdot}2$; Ba = 24·3 per cent.).

6-*Chloro*-o-*benzoicsulphinide* ("6-*Chlorosaccharin*"), 

Difficulty was encountered in the preparation of this saccharin When a dilute aqueous solution of 6-chloro-o-toluenesulphonamid was boiled with the theoretical amount of potassium permanganat solution, oxidation was extremely vigorous, the pink colour rapidl disappearing. Much of the amide was recovered unchanged, an only a trace of sweet substance was produced. It was found tha passing a stream of carbon dioxide through the boiling oxidisin solution resulted in a yield of the saccharin of about 1 per cen After several experiments, the following procedure was found to b satisfactory.

6-... sulphonamide (10·2 grams) and sodium hydroxide (4 gram
ing o-to... ...olved in boiling water (1000 c.c.) and a slow stream
chloride and ...de was passed through the solution, the temperatu
of 2-chloro-p-to... ...d at 96—97° throughout the experiment. Potas
mixture of monoch... (17·4 grams; 10 per cent. excess) dissolved
at 165—169°/33 mm. ...was added very gradually to the sulphonami
on cooling. The soli... ...lour being allowed to disappear before ea
in an almost pure stat... ...seven hours, when the whole of the perma
A considerable impro... ...u decolorised, the liquid was concentrat
effected by using only a sm... ...with sulphur dioxide until the mangan
so rapid that the temper... ...olution. A white precipitate which h
external heating could be ... ...ter remaining overnight, and dissolved
when the weight of the ant... solution (150 c.c.), phenolphthalein v
weight of o-toluenesulphon... ...trated with dilute hydrochloric acid u
however, a reaction did not ...peared. The chlorosulphonamide, be
by allowing the pale yell... ...uenesulphonamide (D.R.-P. 64624),
freezing mixture, the 6-ch... "chlorosaccharin" remained in solut
out, and by filtering at ... ...er remaining several hours at the ordin
present the separation ...

temperature the sulphonamide was filtered off, and dilute hydrochloric acid added to the filtrate. The "chlorosaccharin" was rapidly precipitated as a crystalline mass and was collected after remaining overnight, when 3·1 grams melting at 201—207° were obtained.

The yield was increased by concentrating the mother-liquor, advantage being taken of the great solubility of the sulphonamide and the "chlorosaccharin" in cold acetone to separate them from inorganic matter. The amide was separated as before, and the "chlorosaccharin" finally purified by crystallisation from aqueous acetone. The weight of the latter was 4·0 grams and of unchanged amide (m. p. 172—179°) 4·2 grams. The yield of "chlorosaccharin" from the amide actually used was therefore 62 per cent. (Found N=6·65; C=38·8; H=2·07. $C_7H_4O_3NClS$ requires N=6·4; C=38·6; H=1·84 per cent.).

6-*Chloro-o-benzoicsulphinide* is sparingly soluble in cold, slightly soluble in hot water, and extremely soluble in acetone, from which it crystallises in small, shining plates melting at 210—212°. It is apparently more than half as sweet as saccharin, but has a somewhat astringent taste, except in very great dilution. An aqueous solution of the "chlorosaccharin" (1 in 5000) was unanimously declared by six tasters to be sweeter than a solution of "saccharin" of half the concentration. Opinions differed as to the relative sweetness of solutions of the same concentration. The sodium salt of the "chlorosaccharin" is also very sweet.

Nitration of 6-Chloro-o-toluenesulphonyl Chloride.

To a cold mixture of sulphuric acid (150 c.c.) and nitric acid (45 c.c.; D=1·5), 6-chloro-*o*-toluenesulphonyl chloride (50 grams) was slowly added and the mixture stirred. After a few minutes the nitration began, for there was a rise in temperature, the sulphonyl chloride melted, and the formerly colourless nitration mixture became yellow. The temperature was kept between 20° and 30° by cooling in ice-water, and a further 50 grams of the sulphonyl chloride added at such a rate that these limits were not exceeded. The nitration was complete in two hours, the product of the reaction poured into a litre of cold water, and the heavy oil separated and stirred vigorously with water until free from acid. The oil, which soon became very viscous, was converted into a pale yellow solid by being left overnight in a cold place. It was found that the presence of a small amount of acid seriously hindered solidification. The solid nitration product was powdered and dried on a porous plate in a vacuum over phosphoric oxide. In this way 106 grams

of minute crystals melting at 23—33° were obtained (Found: N=5·29. $C_7H_5O_4NCl_2S$ requires N=5·18 per cent.).

Separation of the Isomerides.

The separation of the isomerides proved to be a far more difficult matter than the separation of the isomerides formed by nitrating 2-chloro-*p*-toluenesulphonyl chloride (this vol., p. 860). Cooling the light petroleum solution resulted in the separation of an oil. However, it was found that a very dilute solution in light petroleum (b. p. 60—80°), when left for six weeks, deposited large, thick prisms and also some needles, the latter being slightly less soluble than the prisms. By taking advantage of this fact, a few grams of each isomeride were obtained in a pure state. The method is, however, extremely laborious and unsatisfactory, owing to the fact that either isomeride tends to separate as an oil when even a small amount of the other isomeride is present in the solution. However, the isolation of a few grams of each isomeride led to the development of the efficient method of separation described below.

The Relative Proportion of the Isomerides in the Mixture.

The percentage of nitrogen in the nitration product shows that either it consists of chloromononitrotoluenesulphonyl chlorides, or unchanged chlorotoluenesulphonyl chloride is present together with chloropolynitrotoluenesulphonyl chlorides. The second alternative is very improbable. With the object of determining the proportion of substances in the nitration product, attempts were made to obtain in the usual way the melting-point curve of the two pure isomerides. Unfortunately, solidification took place so sluggishly that neither the first- nor second-solidification points could be determined with satisfactory accuracy.

However, the eutectic point was determined with some degree of accuracy by melting the two isomerides together, allowing the melt to become quite hard, and then noting the temperature at which the powdered mixture began to soften and adhere to the sides of the tube. It was found that artificial mixtures of the two isomerides softened between 24·5° and 25·5°, and that the nitration product softened at 23—24°. Hence the nitration product consisted almost entirely of the two isomerides which had been obtained in a pure state.

The relative amount of these two isomerides was found by converting them into the easily separable barium salts of the corresponding sulphonic acids. The method is based on the observation

(p. 884) that the barium salt derived from the isomeride that crystallises in needles is very soluble in water and in alcohol (hot and cold), whilst the barium salt from the other isomeride is almost insoluble in boiling alcohol, and only slightly soluble in hot water.

The dry nitrated product (31·50 grams) was gently boiled under reflux with a solution of barium hydroxide (30 grams) in water (450 c.c.) until the oil had disappeared. The solution was just acidified with hydrochloric acid, and then evaporated to dryness on the water-bath. The light brown mass was extracted three times with boiling 99 per cent. alcohol (100 c.c. each time). The first extract was light brown in colour and the third colourless; the last gave only a faint cloudiness with dilute aqueous potassium sulphate solution, and with silver nitrate solution. The alcoholic extract was concentrated to 100 c.c. and allowed to remain overnight, the small quantity of barium chloride and chloronitrotoluenesulphonate precipitated was added to the insoluble mass that had been extracted with alcohol, the alcoholic solution was completely evaporated, and the pale brown residue dried at 120° until the weight was constant (15·05 grams).

The residue insoluble in boiling alcohol was boiled with 200 c.c. of water for some time, and filtered hot. The undissolved barium chloronitrotoluenesulphonate was set aside on a porous plate, the filtrate containing barium chloride and barium chloronitrotoluenesulphonate treated with dilute sulphuric acid to remove the barium, and the filtered solution concentrated on the water-bath until the sulphonic acid began to separate. Water was then added, the solution again evaporated, and this process repeated until the smell of hydrogen chloride could no longer be detected. A small portion of the residue dissolved in dilute nitric acid failed to give a precipitate with silver nitrate solution. The residue, consisting of the sulphonic acid, was dissolved in water (150 c.c.), and the solution neutralised to phenolphthalein by barium hydroxide. The solution was then evaporated to dryness, the light brown residue mixed with the barium chloronitrotoluenesulphonate which had not dissolved with the barium chloride, and the mixture dried at 160° until the weight was constant (22·06 grams).

The 31·50 grams of chloronitrotoluenesulphonyl chloride taken should produce 37·23 grams of barium chloronitrotoluenesulphonates, and 37·11 grams were actually obtained. Hence the percentage of the barium salt soluble in alcohol is 40·42, and of the barium salt insoluble in alcohol 59·27. This result is deduced on the assumption that the third possible isomeride (the amount of which must be very minute—see p. 882) is entirely absent.

6-Chloro-3-nitro-o-toluenesulphonyl Chloride (III).

This sulphonyl chloride crystallises in long, colourless needles melting at 60°. It is readily soluble in cold benzene, ether, or chloroform, and moderately soluble in cold light petroleum, in which it is slightly less soluble than the isomeride formed with it (Found: N=5·3. $C_7H_5O_4NCl_2S$ requires N=5·2 per cent.).

The *sulphonic acid*, prepared by hydrolysing the sulphonyl chloride with hydrochloric acid in a sealed tube, crystallises in very deliquescent, microscopic prisms and is extremely soluble in cold water.

The *sulphonamide* is somewhat soluble in boiling water, but dissolves sparingly in cold water, from which it crystallises in minute needles melting at 181° (Found: N=11·3. $C_7H_7O_4N_2ClS$ requires N=11·2 per cent.).

The *sodium* salt, prepared by neutralising the sulphonic acid or by hydrolysing the sulphonyl chloride with sodium hydroxide solution, is very soluble in hot or cold alcohol, and in water, and from the latter it separates in colourless needles apparently containing four molecules of water of crystallisation (Found: loss at 110—130°=20·3; Na=6·6. $C_7H_5O_5NClSNa,4H_2O$ requires H_2O= 20·8; Na=6·7 per cent. The crystals may be combined with 3½ molecules of water, for $C_7H_5O_5NClSNa,3\frac{1}{2}H_2O$ requires H_2O= 18·7; Na=6·8 per cent.). It decomposes at about 140—150°, long, colourless needles being formed in small quantity, which sublime from the black tar produced and melt and decompose at 270—280°.

The *barium* salt is formed either by neutralising the sulphonic acid with barium hydroxide or by hydrolysing the sulphonyl chloride with barium hydroxide, neutralising with sulphuric acid, filtering, evaporating the filtrate to dryness, extracting the barium salt with hot alcohol, and finally concentrating the alcoholic solution. It crystallises in compact clusters of microscopic needles, which are very soluble in hot or cold water, and in alcohol. The latter solvent retains in solution nearly its own weight of the barium salt at the ordinary temperature. The salt crystallises from its concentrated aqueous solution in small needles containing seven molecules of water of crystallisation. The needles decompose at about 140° with the evolution of a vapour having a strong phenolic smell (Found: loss at 110—125°=16·7; Ba=17·5. $[C_7H_5O_5NClS]_2Ba,7H_2O$ requires H_2O=16·5; Ba=17·9 per cent.).

Determination of the Constitution.—Replacement of the sulphonyl chloride group by hydrogen was attempted by heating the sulphonyl chloride (1 gram) with 7 c.c. of fuming hydrochloric acid at 140—

150° in a sealed tube for seventy-two hours, and it was found that a small quantity of oil was produced, which disappeared, however, with the formation of a clear solution after heating again for twenty-four hours. The oil was evidently unchanged sulphonyl chloride, and the solution contained only a very minute quantity of sulphuric acid.

The *conversion into* 6-*chloro*-3-*nitro*-o-*cresol* (V) was effected by boiling *the chloronitrotoluenesulphonyl chloride* (2 grams) with 10 per cent. sodium hydroxide solution (50 c.c.) for ten hours. The sulphonyl chloride was hydrolysed, forming a pale yellow solution which soon assumed a deep red colour. Only a small quantity of a precipitate was formed and no "bumping" took place. The solution was acidified with hydrochloric acid, whereby it became almost colourless, and was distilled in a current of steam, when the smell of sulphur dioxide was noticed. The yellow solid in the distillate was extracted with ether, the ethereal solution dried with sodium sulphate, and most of the ether removed. As the residual ether evaporated at the ordinary temperature yellow needles were produced melting at 64°. The yield was 0·47 gram (34 per cent.).

This chloronitrocresol gives a red salt with sodium hydroxide, is somewhat volatile with steam, and when heated has a smell recalling that of *o*-nitrophenol. It is noteworthy that it requires about three times as long to distil in a current of steam as the chloronitrocresol described previously (this vol., p. 868). It is very soluble in organic solvents, slightly soluble in cold water, and separates from all solvents in thin, yellow needles melting at 64°. Benzoylation by the Schotten-Baumann method could not be effected (Found : N=7·6. Calc., N=7·5 per cent.).

6-Chloro-3-nitro-*o*-cresol has already been prepared by Noelting (*loc. cit.*), and its properties agree closely with those of the substance described above. In order to place the constitution of the foregoing chloronitrocresol beyond dispute, a specimen of that discovered by Noelting was prepared, and the two substances (m. p. 64°) were found to be identical by a mixed melting-point determination. Hence the formula assigned to the parent chloronitrotoluenesulphonyl chloride is justified.

6-*Chloro*-4-*nitro*-o-*toluenesulphonyl Chloride* (IV).

This compound is very readily soluble in cold benzene, ether, or chloroform, and is moderately soluble in cold light petroleum. It usually crystallises in large, thick prisms, but sometimes separates (especially from light petroleum of low b. p.) in very thin, colour-

less laminæ. Both modifications melt at 63—64° (Found: N=5·2. $C_7H_5O_4NCl_2S$ requires N=5·2 per cent.).

The *sulphonic acid* is obtained by hydrolysing the sulphonyl chloride with water in a sealed tube. It crystallises from cold water, in which it is moderately soluble, as a mass of colourless, flattened needles. It is only slightly hygroscopic, a portion left on a porous plate not completely disappearing in the course of a week.

The *amide* crystallises in minute needles melting at 161°, and is slightly soluble in water and moderately soluble in alcohol. When boiled for a few minutes with ammonia the solution becomes red (Found: N=11·2. $C_7H_7O_4N_2ClS$ requires N=11·2 per cent.).

The *sodium* salt is formed by neutralising the sulphonic acid with sodium hydroxide solution, and when prepared in this way crystallises in colourless plates. When prepared by the hydrolysis of the sulphonyl chloride by sodium hydroxide solution, the salt is obtained quite colourless only with difficulty. It is slightly soluble in boiling alcohol, from which it separates on cooling in flattened needles, and is moderately soluble in water, separating therefrom in plates containing one molecule of water of crystallisation (Found: H_2O= 6·55; Na=8·1. $C_7H_5O_5NClSNa,H_2O$ requires H_2O=6·2; Na=8·2 per cent.).

The *barium* salt formed by neutralising the sulphonic acid with barium hydroxide, is almost insoluble in alcohol. It is somewhat soluble in boiling water, from which it separates on cooling in colourless needles containing one molecule of water of crystallisation (Found: H_2O=3·0; Ba=20·7. $[C_7H_5O_5NClS]_2Ba,H_2O$ requires H_2O=2·75; Ba=20·9 per cent.).

Determination of the Constitution.—The chloronitrotoluene-sulphonyl chloride (2·7 grams) was boiled with 20 per cent. sodium hydroxide solution (25 c.c.) for three hours. The colour quickly became very dark red and a brown powder was precipitated. The solution was cooled and acidified with hydrochloric acid, when a gas was evolved, but the liquid still remained deeply coloured. Part of the solution was distilled in a current of steam, an operation which was accompanied by much frothing, but no organic substance distilled. The other portion of the solution was extracted with ether, which, however, was found to have dissolved no organic substance.

It was noticed that the solution after acidification stained skin a dark yellow, and that the colour was fairly fast to light and soap. For purposes of comparison, 4-nitro-*o*-toluenesulphonyl chloride was heated with sodium hydroxide solution under analogous conditions, and a coloration was produced similar to that described above.

There can therefore be little doubt that the nitro-group in the chloronitrotoluenesulphonyl chloride is in the para-position with respect to the methyl group.

Summary.

(I) The monochlorination of *o*-toluenesulphonyl chloride in the presence of antimony trichloride leads to the formation of a mixture of isomerides, from which 6-chloro-*o*-toluenesulphonyl chloride crystallises in a yield of 38·6 per cent.

(II) The nitration at 20—30° of 6-chloro-*o*-toluenesulphonyl chloride in mixed nitric and sulphuric acids results in the production of 6-chloro-4-nitro-*o*-toluenesulphonyl chloride (about 60 per cent.) and 6-chloro-3-nitro-*o*-toluenesulphonyl chloride (about 40 per cent.).

(III) The sulphonyl chloride group and not the nitro-group in 6-chloro-3-nitro-*o*-toluenesulphonyl chloride is replaceable by the hydroxyl group by boiling with sodium hydroxide solution. This fact may afford an interesting confirmation of the steric hindrance (due to the methyl group) postulated in the theory of Kenner (T., 1920, **117**, 852).

The thanks of the author are due to Professor W. H. Perkin and to Dr. E. Hope for their advice. He also wishes to make acknowledgment to the Ramsay Memorial Fellowship Trust for a Fellowship which has enabled this portion of the research to be completed.

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XCVIII.—*Mitragynine and Mitraversine, Two New Alkaloids from Species of Mitragyne.*

By ELLEN FIELD.

THE natural order of *Rubiaceæ* is rich in alkaloids, and comprises amongst others the genera *Cinchona*, *Remijia* (yielding Cuprea bark), *Psychotrea* (*Ipecacuanha*), and *Corynanthe* (yielding yohimbine). The present investigation deals with some species of the genus *Mitragyne* of the same order.

A quantity of an alcoholic extract of the leaves of *M. speciosa*, Korth., was supplied by Professor G. Barger, for which he was

indebted to Dr. P. P. Laidlaw and the National Medical Research Council. The leaves were obtained from the Malay States and were identified at Kew through the kindness of the Director of the Royal Gardens. This tree has also been recorded from Borneo, the Philippine Islands, and New Guinea. The leaves have now been found to contain an alkaloid, $C_{22}H_{31}O_5N$, for which the name *mitragynine* is suggested.

Alkaloids have been stated to be present in two other species of *Mitragyne*. The bark of *M. africana*, Korth. (Écorce de Xosse), is used in Senegal as a febrifuge, and is believed to contain an alkaloid (Wehmer, "Die Pflanzenstoffe," 1911, p. 728, according to Dragendorff, "Die Heilpflanzen," 1898). Hooper (*Pharm. J.*, 1907, **78**, 453) isolated a crystalline alkaloid from the leaves of *M. parvifolia*, Korth., in a yield of 0·15 per cent. I was unable to obtain any alkaloid from a small specimen of the leaves of *M. parvifolia* at my disposal, but found, on the other hand, a crystalline alkaloid in the leaves of *M. diversifolia*, Hook. f., kindly sent to Professor Barger by Mr. E. D. Merrill, formerly botanist in the Bureau of Science, Manila. For this alkaloid the name *mitraversine* is suggested.

According to Redley (quoted by Hooper, *loc. cit.*) *Mitragyne speciosa* is used in Perak against the opium habit, whilst, according to Dr. P. P. Laidlaw, mitragynine is a local anæsthetic, which finding is of interest, since the alkaloid contains an ester grouping. Its formula may apparently be resolved to $C_{17}H_{22}N(OMe)(CO_2Me)_2$, and it is probably an indole derivative.

EXPERIMENTAL.

Mitragynine, $C_{22}H_{31}O_5N$, *from* M. speciosa.

Preliminary experiments had shown that the salts of the alkaloid with strong mineral acids were apt to form gels and to be precipitated from aqueous solution by excess of the acid. Therefore the residue left by evaporating the alcoholic extract of the leaves was dissolved in glacial acetic acid, and by addition of water a large quantity of resin and chlorophyll was precipitated. In some experiments, the filtrate was purified by means of lead acetate. On making the solution alkaline with ammonia, an amorphous precipitate separated. Ten grams of this (from 2 kilos. of leaves) were dissolved in 75 c.c. of 20 per cent. acetic acid and a hot solution of 6 grams of picric acid in 300 c.c. of water added. The yield of crude picrate was 15 grams. It was crystallised from 100 c.c. of boiling glacial acetic acid, yielding 6 grams of crystals. The yield of the pure picrate is thus 0·3 per cent. of the weight of the

leaves, corresponding with 0·2 per cent. of pure base; the content is doubtless higher, and other alkaloids appear to be present, as the amount of viscid base obtained in several experiments was 0·5 per cent.

Mitragynine picrate, $C_{22}H_{31}O_5N,C_6H_3O_7N_3$, is the only salt suitable for the initial purification of the alkaloid. It forms orange-red, slender needles from methyl alcohol, and melts at 223—224° (Found: C=54·2, 54·3; H=5·5, 5·6; N=9·4; picric acid [by nitron]=35·3. $C_{22}H_{31}O_5N,C_6H_3O_7N_3$ requires C=54·3; H=5·5; N=9·1; picric acid=37·2 per cent.). The free *alkaloid* was obtained by dissolving the picrate in boiling glacial acetic acid and pouring the solution into dilute ammonia and filtering while still hot so as to avoid separation of ammonium picrate. The washed precipitate was suspended in dilute ammonia and shaken with ether. It was an amorphous, colourless solid, and could not be obtained crystalline. The ethereal solution had a green fluorescence.

Mitragynine distils unchanged at 230—240°/5 mm., the distillate forming white, amorphous crusts, m. p. 102—106°, yielding a picrate identical with that described above. Various salts were prepared by dissolving the alkaloid in ether and adding an ethereal solution of an acid. The salts with mineral acids have a great tendency to gelatinise; the hydrochloride was crystallised by careful addition of dry ether to its solution in 95 per cent. alcohol; it formed rhomb-shaped leaflets, m. p. 243°. The oxalate and tartrate were likewise unsatisfactory, but the acetate, mono-, and trichloro-acetates were obtained pure more easily.

The *acetate* was prepared by dissolving the base (recovered from the picrate) in ether and adding glacial acetic acid until a permanent precipitate was just formed. In a few hours the acetate separated (3·7 grams from 6 grams of pure picrate). Recrystallised from glacial acetic acid and ether, it formed slender, silky needles, m. p. 142°.

The *trichloroacetate* is, after the picrate, the salt most easily obtained pure of those investigated. It forms needles from acetone and ether, m. p. 157° (Found: Cl=19·35. $C_{22}H_{31}O_5N,CCl_3{\cdot}CO_2H$ requires Cl=19·25 per cent.).

Mitragynine contains three methoxy-groups, but no *N*-methyl group (Found, for base regenerated from pure picrate: MeO=21·8; 3MeO requires 23·9 per cent.; found, for acetate: MeO=17·8, 18·8; 3MeO requires 20·7 per cent. No more silver iodide was obtained at 340° by Herzig and Meyer's method). The product of the action of hydriodic acid and of hydrobromic acid was insoluble in most organic solvents, including pyridine and nitrobenzene, and decomposed at 380°.

Action of Alkali on Mitragynine Acetate.

One gram of the acetate was boiled under reflux on the water-bath with 20 c.c. of alcoholic 2*N*-sodium ethoxide. The substance gradually dissolved. After three hours, the solution was cooled and neutralised with the calculated quantity of alcoholic hydrogen chloride. The sodium chloride which separated was filtered off, and the filtrate and alcoholic washings were concentrated to small bulk. The residue consisted of an amphoteric substance insoluble in ether, soluble in ammonia and in acid, and of a substance which dissolved in ether. The latter furnished a cream-coloured sublimate at 250°/2 mm., which gave an intense violet coloration when boiled with vanillin and hydrochloric acid, indicating the presence of an indole derivative. The amphoteric substance was washed free from alcohol by ether and dried in a vacuum. This substance contained one methoxy-group, so that two such groups had been eliminated by the alkaline hydrolysis (Found: MeO=8·3. $C_{19}H_{24}O_4N[OMe]$ requires MeO=8·6 per cent.). The product formed by hydrolysis with sodium ethoxide is therefore a dicarboxylic acid of the formula $C_{17}H_{22}N(OMe)(CO_2H)_2$ (assuming that the alkyl groups eliminated are methyl groups). The substance *was amorphous, readily soluble in alcohol, but not in ether, and* melted at 280°. It yielded no crystalline derivatives; in particular, the picrate, soluble in hot water, separated in a gelatinous condition on cooling. With a view to eliminate the carboxyl groups, 0·5 gram of the product of hydrolysis with sodium ethoxide was mixed with 2 grams of calcium oxide and heated in a metal-bath at 2 mm. pressure. About 0·2 gram of a glassy distillate was obtained, which dissolved in ether to a yellow solution, leaving on evaporation a viscous, green oil, no longer entirely soluble in ether. This base gave an amorphous hydrochloride and a red picrate, which was obtained crystalline from methyl alcohol in small quantity and melted fairly sharply at 218°. In subsequent experiments the yield of the red picrate could not be improved, and sometimes none was obtained. There is reason to believe that mitragynine is an indole derivative, or at least undergoes decomposition with the formation of such a substance. Apart from the coloration of the decomposition product referred to above, with vanillin and hydrochloric acid, and the formation of a red picrate, this is suggested by the fact that the acid resulting by hydrolysis of mitragynine gives the pinewood reaction on heating with soda-lime, and particularly on heating with zinc dust. Mitragynine itself, on boiling with vanillin and hydrochloric acid, gives a purple colour, and when concentrated sulphuric acid is poured under a solution of

mitragynine containing glyoxylic acid, the sulphuric acid is coloured blue, reminiscent of the Adamkiewicz reaction for tryptophan.

Mitraversine, $C_{22}H_{26}O_4N_2$(?), *from* M. diversifolia.

One kilo. of leaves was percolated with 20 litres of 92 per cent. alcohol; after evaporation of the alcohol, the residue was dissolved in the minimum quantity of glacial acetic acid, and the solution poured into water. After filtration, the filtrate was made alkaline with ammonia, and extracted with ether. The ether (4 litres) was extracted twenty times with 10 per cent. acetic acid, the extracts, when made alkaline, giving a flocculent precipitate, which crystallised from methyl alcohol in a total yield of 0·27 per cent. of the weight of the leaves employed.

Mitraversine melts at 237°, is slightly soluble in boiling water and readily soluble in dilute sodium hydroxide solution and in dilute acids (Found: C=68·4; H=7·0; N=7·6. $C_{22}H_{26}O_4N_2$ requires C=69·1; H=6·8; N=7·3 per cent.). The molecular weight was determined by Barger's microscopic method (0·1526 in 5 c.c. of pyridine=0·0093 molar; M=328. $C_{22}H_{26}O_4N_2$ requires M=382). Mitraversine contains two methoxy-groups (Found: MeO=14·6. $C_{20}H_{20}O_2N_2[OMe]_2$ requires MeO=16·2 per cent.). The *hydrochloride* forms rhomb-shaped leaflets melting at 208—210° (Found: Cl=7·7. $C_{22}H_{26}O_4N_2$,HCl requires Cl=8·5 per cent.). Owing to the small amount of material available, the formula could not be settled definitely.

The author wishes to express her indebtedness to the Department of Scientific and Industrial Research for a grant which enabled her to carry out this research, and also to thank Professor G. Barger for advice during the course of the work, and Dr. A. J. Ewins for some analytical results.

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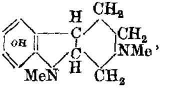
XCIX.—*A New Degradation Product of Physostigmine.*

By EDGAR STEDMAN.

IN the course of an investigation of the constitution of physostigmine, an attempt was made to prepare the methyl ether of eseroline methiodide by the action of methyl iodide and sodium ethoxide

on eseroline methiodide, $C_{14}H_{21}ON_2I$. In place of the expected ether, a compound of the composition $C_{10}H_{17}ON_2I$ was obtained; *the molecule has therefore suffered an at present inexplicable nett loss of* C_4H_4. (If one methyl group were added, C_5H_8 has been eliminated from the original molecule.) Straus (*Annalen*, 1913, **401**, 358) has suggested the following provisional constitution for eseroline:



but it is difficult to conceive how such a compound could lose four or five carbon atoms and still retain two nitrogen atoms. The carbon atoms cannot come from the benzene ring, for the new iodide, $C_{10}H_{17}ON_2I$, still gives an indole derivative on distillation; and if the piperidine ring were broken down, its nitrogen would be eliminated. It is not inconceivable that eseroline (and physostigmine) do not contain a preformed pyrrole ring at all, but possibly a heterocyclic ring with two nitrogen atoms, which survives the gentle treatment with alcoholic sodium ethoxide and methyl iodide, but is broken down on heating eseroline methiodide at a much higher temperature (the second way in which Straus obtained physostigmol, an indole derivative). Max and Michel Polonovski (*Bull. Soc. chim.*, 1918, [iv], **23**, 336) are convinced that eserolinium hydroxide (Straus's first method) does not undergo simple fission into dimethylamine and physostigmol, but that it is formed by a complete disintegration of the molecule.

It is thought that the methiodide now obtained will be a suitable starting-point for further investigation of the constitution of the alkaloid. Experiments are also in progress to elucidate the mechanism of its formation.

EXPERIMENTAL.

Preparation of the Compound $C_{10}H_{17}ON_2I$.—The following is an example of several similar experiments: Thirteen c.c. of a solution of 0·5 gram of sodium in 50 c.c. of ethyl alcohol were placed in a flask fitted with a reflux condenser and the air was displaced from the apparatus by means of a current of hydrogen. One gram of eseroline methiodide, prepared by Straus's modification of Salway's method (*Annalen*, 1913, **401**, 350), was then added. When solution had taken place, excess of methyl iodide was added through the condenser and the flask heated on the water-bath for one and

half hours, a slow stream of hydrogen being passed through the apparatus continuously. During this period a crystalline solid separated. The solution was now cooled in ice, causing a further separation of crystals, and filtered (yield 0·3 gram). When recrystallised from methyl alcohol, the substance formed plates which commenced to darken at about 210° and melted at 235° with decomposition and evolution of a gas (Found: C=39·08; H=5·51; N=9·02 *; I=41·74, 42·19. $C_{10}H_{17}ON_2I$ requires C=38·96; H=5·52; N=9·09; I=41·23 per cent.).

Estimation of Methoxy- and N-Methyl Groups.—A methoxyl estimation by Zeisel's method on 0·1111 gram of substance gave a negative result, but when the temperature was raised for the estimation of *N*-methyl groups by Herzig and Meyer's method a separation of silver iodide began at 160°, and on a second distillation a further separation occurred at 250°. A third distillation, during which the temperature was finally raised to 300°, produced no result (Found: Me=14·04. 3Me in $C_{10}H_{17}ON_2I$ requires Me=14·61 per cent.).

As methyl iodide began to be given off at as low a temperature as 160°, it is as yet not quite certain whether all three methyl groups are attached to nitrogen or whether one methoxy-group is present.

Attempted Degradation of the Compound.—The iodine was readily removed by treating an aqueous solution of 0·3 gram of the compound with moist silver oxide. After filtration, the solution was evaporated under diminished pressure, leaving the quaternary hydroxide as a brown syrup. This was distilled under diminished pressure. Decomposition commenced at about 160°/12 mm., a volatile amine being evolved, and at 220°/12 mm. an almost colourless syrup was collected. On admission of air into the apparatus, however, this appeared to polymerise partly. The remainder was dissolved in ether, but decomposed on evaporation on the water-bath, and was evidently very unstable. So far, the volatile amine has not been collected in sufficient quantity to identify it.

The substance $C_{10}H_{17}ON_2I$ itself does not give any indole reactions, but when it is heated above its melting point under atmospheric pressure gases and an oily distillate are formed, giving an indole reaction with *p*-dimethylaminobenzaldehyde. The vapours formed give the pinewood reaction.

In conclusion, the author desires to express his thanks to Prof. G. Barger, F.R.S., for his advice and assistance during the course

* Micro-Dumas according to Dubsky. 12·334 mg. gave 0·960 c.c. N_2 at 16° and 757 mm.

: these experiments. The physostigmine was purchased out of a rant from the Earl of Moray Research Fund of this University, for which grateful acknowledgment is made.

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C.—*Dinitrotolylhydrazines.*

By OSCAR LISLE BRADY and JOHN HERBERT BOWMAN.

GIUA (*Gazetta*, 1919, **49**, ii, 166) has described the action of hydrazine hydrate on 3 : 4 : 6- and 2 : 3 : 4-trinitrotoluenes. In the former case, he obtained 4 : 6-dinitro-*m*-tolylhydrazine, but in the latter he did not isolate the hydrazine, but a compound richer in nitrogen, melting and decomposing at 150°, which he suggests may be a nitronitrosotolylhydrazine or a nitrohydroxymethylbenzotriazole,

$$NO_2{\cdot}C_6H_2Me{<}{\genfrac{}{}{0pt}{}{\overline{\quad\;\; N}}{N(OH)}}{>}N.$$

This reaction had been observed by one of us before the publication of Giua's work, but had not been fully investigated. As the results obtained at that time were at variance with those of Giua with respect to the action of hydrazine hydrate on 2 : 3 : 4-trinitrotoluene, the reaction has been studied further and extended to the other trinitrotoluenes containing a mobile nitro-group.

It has been found that by the action of hydrazine hydrate on 2 : 3 : 4-, 2 : 3 : 5-, and 3 : 4 : 5-trinitrotoluenes the corresponding dinitrotolylhydrazines are formed, as in the case of 3 : 4 : 6-trinitrotoluene. The compounds have been oriented by oxidation of the hydrazino-group to hydrogen by means of cupric acetate and identification of the dinitrotoluene produced. In every case it was found that the nitro-group replaced by the hydrazine residue was the same as that displaced by ammonia and other amines.

The dinitrotolylhydrazines are readily crystallisable substances which undergo the usual reactions of arylhydrazines. Oxidation with cupric chloride and with iodine replaces the hydrazino-group by chlorine and iodine respectively. They form hydrazones with aldehydes and ketones, which, on account of their high, sharp melting points, their sparing solubility, and the ease with which they may be prepared and crystallised, are very convenient for the identification of these substances.

With 2 : 3 : 6-trinitrotoluene, the reaction did not proceed

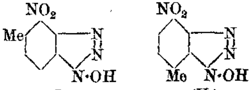
the normal manner (compare Drew, T., 1920, **117**, 1616) and an oily product was obtained, which has not been further investigated owing to lack of material. This result, however, is in accord with the work of other investigators who experienced a similar difficulty in replacing the nitro-group with ammonia (Körner and Contardi, *Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 339).

Some explanation is necessary of the discrepancy between our results and those of Giua in the case of 2 : 3 : 4-trinitrotoluene. In the preparation of 4 : 6-dinitro-*m*-tolylhydrazine from 3 : 4 : 6-trinitrotoluene, Giua used 2 grams of 50 per cent. hydrazine hydrate for 2·27 grams of the trinitrotoluene, but in the case of the 2 : 3 : 4-compound, only 1·5 grams of the hydrate, that is, one and a half molecular proportions. As the reaction that takes place is

$$C_6H_2Me(NO_2)_3+2NH_2{\cdot}NH_2,H_2O \longrightarrow C_6H_2Me(NO_2)_2{\cdot}NH{\cdot}NH_2+HN_3+4H_2O,$$

this amount is insufficient. Using Giua's quantities, a substance melting at 154° was obtained, and it was found that this was a mixture of the dinitrotolylhydrazine and the hydrazine salt of nitrohydroxymethylbenzotriazole. Owing to the sparing solubility of this hydrazine salt in cold alcohol, it cannot easily be removed by crystallisation of the mixture from this solvent, the method of purification employed by Giua, but it can readily be got rid of by washing with cold water.

Giua's substance cannot be the benzotriazole compound, as this has now been prepared by the action of excess of hydrazine hydrate or of alcoholic sodium hydroxide on the dinitrotolylhydrazine and found to be quite different from the compound described by him. The orientation of the benzotriazole derivative has not yet been



(I.) (II.)

established; the compound may be either 4-nitro-1-hydroxy-5-methyl-1 : 2 : 3-benzotriazole (I) or 4-nitro-1-hydroxy-7-methyl-1 : 2 : 3-benzotriazole (II).

A fuller description of compounds of this class will be made the subject of a further communication.

Another possibility was that the azoimide formed in the reaction had reacted with the excess of trinitrotoluene to give the triazo-compound, $C_6H_2Me(NO_2)_2{\cdot}N_3$. This compound has also been prepared and found to melt at 89°.

A dinitrotolylhydrazine is mentioned by Borsche and Fiedler (*Ber.*, 1913, **46**, 2129), but they give no description or analysis. Their compound was obtained by the action of hydrazine hydrate on a compound supposed by these authors to be 3-chloro-2 : 4-dinitrotoluene melting at 73°. This compound was obtained as a by-product in the nitration of *m*-chlorotoluene and its structure assigned by analogy, on account of its similarity to 1-chloro-2 : 6-dinitrobenzene. We have, however, prepared 3-chloro-2 : 4-dinitrotoluene by the action of cupric chloride on 2 : 4-dinitro-*m*-tolylhydrazine and found it to melt at 93°. It seems probable that Borsche and Fiedler's compound was 3-chloro-2 : 6-dinitrotoluene, which Körner and Contardi prepared (*loc. cit.*) and found to melt at 75°. The formation of this compound in small quantities in the nitration of *m*-chlorotoluene rather than the 2 : 4-dinitro-derivative might be expected from the course of the nitration of aceto-*m*-toluidide. Here the main product of nitration is the 4 : 6-dinitro-derivative, a small quantity of the 2 : 6-, but no 2 : 4-dinitro-compound being formed (Cook and Brady, T., 1920, **117**, 750). Similarly, the lack of reactivity of the chlorine atom noticed by Borsche and Fiedler is in accordance with the observations of Körner and Contardi and others on the abnormal behaviour of 2 : 3 : 6-trinitrotoluene. It appears, therefore, that Borsche and Fiedler's dinitrotolylhydrazine and the benzotriazole they prepared from it (decomposing at 110—170°), which Giua in a later paper (*Gazzetta*, 1920, **50**, ii, 327) suggests might be identical with his compound melting at 150°, have been incorrectly oriented and are 2 : 3 : 6-trisubstituted derivatives.

EXPERIMENTAL.

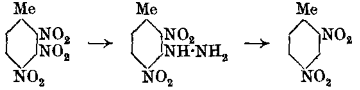
2 : 4-*Dinitro*-m-*tolylhydrazine*.

Eleven grams of 2 : 3 : 4-trinitrotoluene were dissolved in 150 c. of boiling alcohol and 10 c.c. of hydrazine hydrate (50 per cent diluted with 20 c.c. of alcohol added. The mixture, which acquir a deep red tint, was cooled at once in a stream of water, when t hydrazine separated in red crystals. If the mixture is boiled, t excess of hydrazine will react with the dinitrotolylhydrazine give the benzotriazole, with consequent loss of yield; under t above conditions, however, an 80 to 90 per cent. yield of an alm pure product is obtained. 2 : 4-*Dinitro*-m-*tolylhydrazine* crystalli from boiling alcohol or benzene in long, red, prismatic need melting at 170° (Found: N=26·8. $C_7H_8O_4N_4$ requires N=2 per cent.). The hydrazine is soluble in warm 10 per cent. hyd

chloric acid, but the hydrochloride is readily hydrolysed and dilution of the acid solution causes precipitation of the base.

Acetyl-2 : 4-dinitro-m-tolylhydrazine.—The above hydrazine was dissolved in four to five times its weight of warm acetic anhydride. On cooling, the *acetyl* derivative separated. It crystallised from alcohol in long, brilliant yellow, rhombic needles melting and decomposing at 193° (Found: N=22·3. $C_9H_{10}O_5N_4$ requires N=22·0 per cent.).

Orientation of 2 : 4-Dinitro-m-tolylhydrazine.—The hydrazine was heated on the water-bath for thirty minutes in glacial acetic acid with excess of cupric acetate. The mixture was cooled, diluted with a large excess of water, and after leaving for some time filtered. The solid was extracted with hot alcohol to eliminate inorganic matter and the dinitrotoluene precipitated from the solution by dilution with water. On crystallisation, it melted at 70° and did not depress the melting point of 2 : 4-dinitrotoluene (m. p. 70·5).



3-*Chloro-2 : 4-dinitrotoluene*.

Five grams of the hydrazine were dissolved in boiling alcohol and 20 grams of cupric chloride slowly added thereto, when copious evolution of nitrogen occurred. The mixture was cooled and filtered, but a certain amount of cuprous chloride remained in solution and was precipitated on dilution with the chloro-compound, from which it was difficult to remove. Consequently, the alcoholic solution was treated with concentrated hydrochloric acid and a little hydrogen peroxide on the water-bath for an hour to reoxidise the cuprous salt. The solution was then diluted and the precipitate recrystallised from alcohol, when **3-*chloro*-2 : 4-*dinitrotoluene*** separated in long, silky, pale yellow needles melting at 92° (Found: Cl=16·2. $C_7H_5O_4N_2Cl$ requires Cl=16·4 per cent.).

3-*Iodo-2 : 4-dinitrotoluene*.

A solution of 3 grams of the hydrazine in boiling alcohol was treated with excess of iodine. The mixture was boiled for thirty minutes, the excess of iodine removed with sulphurous acid, and the compound precipitated by the addition of water. **3-*Iodo*-2 : 4-*dinitrotoluene*** crystallises from alcohol in yellow leaflets melting at 117° (Found: N=9·4. $C_7H_5O_4N_2I$ requires N=9·1 per cent.)

4-*Nitro*-1-*hydroxy*-5 (or 7)-*methyl*-1 : 2 : 3-*benzotriazole*.

A hot alcoholic solution of 2 grams of 2 : 4-dinitro-*m*-tolylhydrazine was boiled for five minutes with 2 c.c. of 50 per cent. hydrazine hydrate. Orange-yellow crystals of the hydrazine salt began to separate at once, the quantity increasing when the mixture was cooled. The crystals of the salt were dissolved in water and the solution was acidified with dilute hydrochloric acid, when the benzotriazole derivative was precipitated. It crystallised from hot alcohol in very pale yellow, hexagonal prisms containing a molecule of water of crystallisation, which was lost at 100°, the componnd then acquiring a lemon-yellow colour. By heating in a melting-point tube, the water was first driven off and the anhydrous compound then melted and decomposed at 205° (Found: N=26·6; H_2O=8·7. $C_7H_6O_3N_4,H_2O$ requires N=26·4; H_2O=8·5 per cent.).

This compound may also be obtained by treating a hot, alcoholic solution of the hydrazine with 10 per cent. alcoholic sodium hydroxide until a permanent red colour is obtained. On cooling, the sodium salt crystallises and may be decomposed with acids as before.

The benzotriazole derivative is slightly soluble in water, giving a brilliant yellow solution, but is less soluble in dilute hydrochloric acid; it is readily soluble in caustic alkalis and in warm sodium carbonate solution, giving in each case deep orange-red solutions When heated rapidly, it deflagrates and in a closed tube explode violently. The hydrazine salt crystallises in orange needles sparingly soluble in cold alcohol, but readily soluble in water. On heating, it deflagrates violently (Found: N=37·4. $C_7H_6O_3N_4,N_2H$ requires N=37·2 per cent.).

2 : 4-*Dinitro*-m-*tolylazoimide*.

To a hot, alcoholic solution of 2 grams of 2 : 3 : 4-trinitrotoluen 0·6 gram of sodium azide dissolved in alcohol was added. Th solution assumed a red tint, and after boiling for a few minut was diluted somewhat and cooled. The *azoimide* which separat was crystallised from alcohol, when it was obtained in silve leaflets which turned pale green on exposure to light and melt at 89°; on stronger heating, it decomposed quietly and showed tendency to explode (Found: N=31·5. $C_7H_5O_4N_5$ requi N=31·3 per cent.).

2 : 4-*Dinitro*-m-*tolylhydrazones*.

The hydrazones were prepared by adding a slight excess of alcoholic solution to a hot, alcoholic solution of

hydrazine, heating on the water-bath for some time, diluting somewhat with water, cooling, and crystallising the product from alcohol. In some cases, the hydrazone began to separate from the hot liquid, or crystallised on cooling without the addition of water, but the same process was adopted in each case for simplicity.

Formaldehyde-2 : 4-*dinitro*-m-*tolylhydrazone* crystallises in fine yellow needles melting at 132° (Found: N=25·0. $C_8H_8O_4N_4$ requires N=25·0 per cent.).

Acetaldehyde-2 : 4-*dinitro*-m-*tolylhydrazone* is a yellow, crystalline powder melting at 112° (Found: N=24·0. $C_9H_{10}O_4N_4$ requires N=23·5 per cent.).

n-*Propaldehyde*-2 : 4-*dinitro*-m-*tolylhydrazone* crystallises in long, orange-yellow tables melting at 100° (Found: N=22·2. $C_{10}H_{12}O_4N_4$ requires N=22·2 per cent.).

n-*Butaldehyde*-2 : 4-*dinitro*-m-*tolylhydrazone* forms orange-red prisms melting at 86° (Found: N=21·3. $C_{11}H_{14}O_4N_4$ requires N=21·1 per cent.).

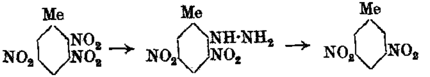
Benzaldehyde-2 : 4-*dinitro*-m-*tolylhydrazone* forms orange-red needles melting at 188° (Found: N=18·8. $C_{14}H_{12}O_4N_4$ requires N=18·7 per cent.).

Acetone-2 : 4-*dinitro*-m-*tolylhydrazone* crystallises in long, orange-red needles melting at 102° (Found: N=22·6. $C_{10}H_{12}O_4N_4$ requires N=22·2 per cent.).

Methyl ethyl ketone 2 : 4-*dinitro*-m-*tolylhydrazone* forms orange-yellow needles melting at 94° (Found: N=21·4. $C_{11}H_{14}O_4N_4$ requires N=21·1 per cent.).

3 : 5-*Dinitro*-o-*tolylhydrazine*.

Two grams of 2 : 3 : 5-trinitrotoluene were dissolved in 25 c.c. of boiling alcohol and 2 c.c. of hydrazine hydrate diluted with 10 c.c. of alcohol added. The mixture was at once cooled and the precipitated hydrazine crystallised from alcohol, in which it was sparingly soluble. 3 : 5-*Dinitro*-o-*tolylhydrazine* separates in orange, flaky needles melting and decomposing at 169° (Found: N=26·9. $C_7H_8O_4N_4$ requires N=26·4 per cent.). The compound was oriented by oxidation with cupric acetate (see above), the dinitrotoluene produced being the 3 : 5-isomeride.



Acetone-3 : 5-*dinitro*-o-*tolylhydrazone*.—An alcoholic solution of the above hydrazine was boiled for a few minutes with a slight

excess of acetone. On diluting with water and cooling, the hydrazone separated and was crystallised from alcohol, when it formed scarlet needles melting at 128° (Found: N=22·5. $C_{10}H_{12}O_4N_4$ requires N=22·2 per cent.).

Benzaldehyde-3 : 5-*dinitro*-o-*tolylhydrazone*.—An alcoholic solution of the hydrazine was boiled with a slight excess of benzaldehyde. The derivative began to separate from the hot liquid, which was cooled, and the solid crystallised from a mixture of acetone and alcohol, when it separated as a crystalline, vermilion powder melting at 194° (Found: N=18·7. $C_{14}H_{12}O_4N_4$ requires N=18·7 per cent.).

3 : 5-*Dinitro*-p-*tolylhydrazine*.

This compound was prepared from 3 : 4 : 5-trinitrotoluene in the same way as the dinitro-*o*-tolylhydrazine. In this case, however, there was a greater tendency to form the hydrazine salt of the benzotriazole, which, on account of its sparing solubility, was difficult to remove. Three crystallisations from alcohol, however, gave the pure hydrazine in lustrous, copper-coloured plates. These crystals, on grinding, gave a brown powder which turned bright red at 130° and melted at 139°. The red substance, on cooling, did not change its colour, but crystallisation from alcohol produced the original copper-coloured compound (Found: N=26·7. $C_7H_8O_4N_4$ requires N=26·4 per cent.). This compound was oriented as before by oxidation with cupric acetate to 3 : 5-dinitrotoluene.

Benzaldehyde-3 : 5-*dinitro*-p-*tolylhydrazone*, prepared in the same way as the dinitro-o-tolyl derivative, crystallises from acetone in scarlet leaflets melting at 214° (Found: N=18·8. $C_{14}H_{12}O_4N_4$ requires N=18·7 per cent.).

4-*Nitro*-1-*hydroxy*-6-*methyl*-1 : 2 : 3-*benzotriazole*.

The above hydrazine in alcohol was boiled with hydrazine hydrate for some minutes. The hydrazine salt, which crystallised on cooling, was dissolved in hot water, the solution acidified with dilute hydrochloric acid, and cooled. The *benzotriazole* crystallised and was purified by crystallisation from dilute alcohol, when it separated in very pale yellow, silky needles which began to decompose above 200° but did not melt at 230° (Found: N=28·9. $C_7H_6O_3N_4$ requires N=28·9 per cent.). The hydrazine salt is sparingly soluble in cold, but readily soluble in hot water.

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CI.—*Studies in the Anthracene Series. Part I.*

By Edward de Barry Barnett and James Wilfred Cook.

Several cases have been recorded in the literature in which the formation of a pyridinium salt is accompanied by a weakening of the pyridine ring, so that when the salt is treated with a basic substance the ring is opened and a derivative of glutaconaldehyde formed. Thus König and Bayer (*J. pr. Chem.*, 1911, [ii], **83**, 325) in a preliminary note give a list of some thirty-three organic and inorganic halogen compounds which appear to yield additive compounds with pyridine in which the ring system is so weakened that it is broken open by treatment with aniline. Similar reactions have been described by Reitzenstein and Brüning (*ibid.*, 1911, [ii], **83**, 97) in the cases of the pyridinium salts obtained from di-*o*-tolyloxaliminochloride, tolane dichloride, and benzanilideimide-chloride, but the most detailed investigation of this type of reaction has been carried out by Zincke and his students in the case of 2 : 4-dinitrophenylpyridinium chloride (Zincke, *Annalen*, 1904, **330**, 361; **333**, 296; 1905, **338**, 107; **341**, 365) and similarly constituted salts (Zincke and Krollpfeiffer, *Annalen*, 1914, **408**, 285; Zincke and Weisspfenning, *J. pr. Chem.*, 1910, [ii], **82**, 1; 1912, [ii], **85**, 207). Although the products formed depend to some extent on the experimental conditions, the results obtained by these investigators can be briefly summarised as follows.

(1) Heating with water leads to the replacement of the pyridinium group by a hydroxyl group; 2 : 4-dinitrophenylpyridinium chloride, for example, when heated with water at 150° yields 2 : 4-dinitrophenol. This reaction takes place particularly easily in the case of pyridinium salts of weak acids. In the example quoted above, the reaction takes place at 100° in the presence of sodium acetate, and at the ordinary temperature in the presence of sodium nitrite.

(2) The action of sodium hydroxide, sodium carbonate, or ammonia leads to an opening of the pyridine ring with the production of highly coloured substances which have the alternative formulæ ArN:CH·CH:CH·CH:CH·OH or ArNH·CH:CH·CH:CH·CHO, and hence must be regarded as monoanils of glutaconaldehyde.

(3) The action of primary and secondary aliphatic amines is very similar to that of the alkalis, except that the excess of the amine combines with the monoanil to form a dianil of the structure ArN:CH·CH:CH·CH:CH·NHR or ArNH·CH:CH·CH:CH·CH:NR.

(4) The action of primary and secondary aromatic amines leads to the complete displacement of the cyclic nitrogen atom, the

reaction products in the case of 2 : 4-dinitrophenylpyridinium chloride being 2 : 4-dinitroaniline and a dianil of glutaconaldehyde. Some primary aromatic amines, however, such as 2 : 4-dichloroaniline and *o*-, *m*-, and *p*-nitroaniline, do not react.

An investigation of the properties of pyridinium salts containing the anthracene ring system seemed to be of interest, and the present communication contains an account of the behaviour of 9 : 10-dihydroanthraquinyldipyridinium dibromide.

As would be expected, this salt is not very stable and on boiling with water both pyridinium groups are easily split off, the resulting 9 : 10-dihydroanthraquinol at once losing water and then becoming ketonised to anthrone (Kurt Meyer, *Annalen*, 1911, **379**, 37):

$$C_6H_4\left<\begin{matrix}CH(C_5H_5NBr)\\CH(C_5H_5NBr)\end{matrix}\right>C_6H_4 \rightarrow C_6H_4\left<\begin{matrix}CH(OH)\\CH(OH)\end{matrix}\right>C_6H_4 \rightarrow C_6H_4\left<\begin{matrix}CH\\C(OH)\end{matrix}\right>C_6H_4$$

$$\downarrow$$

$$C_6H_4\left<\begin{matrix}CH_2\\CO\end{matrix}\right>C_6H_4.$$

The yields are almost quantitative, and as the dipyridinium dibromide is easily obtained the process is the most convenient one for preparing anthrone. In this reaction the replacement of both pyridinium groups must take place simultaneously and not successively, for, as will be seen later, when only one pyridinium group is replaced by a hydroxyl group, the resulting compound (I) at once loses water and passes into the perfectly stable anthranylpyridinium bromide (II). In the presence of acids, however, the replacement appears to take place in two steps, as but little anthrone is obtained when the dipyridinium dibromide is boiled with sulphurous acid, and if first boiled with an alcoholic solution of hydrogen chloride subsequent boiling with water yields no anthrone at all. From the solutions thus obtained the addition of picric acid leads to the precipitation of anthranylpyridinium picrate. The action of cold sodium hydroxide or ammonia solution, or of a primary or secondary aliphatic amine, leads to the replacement of only one pyridinium group by the hydroxyl group:

$$C_6H_4\left<\begin{matrix}CH(C_5H_5NBr)\\CH(C_5H_5NBr)\end{matrix}\right>C_6H_4 \rightarrow C_6H_4\left<\begin{matrix}CH(C_5H_5NBr)\\CH(OH)\end{matrix}\right>C_6H_4 \rightarrow$$

(I.)

$$C_6H_4\left<\begin{matrix}C(C_5H_5NBr)\\CH\end{matrix}\right>C_6H_4,H_2O.$$

(II.)

Analysis of the resulting salt shows that it has the empirical formula $C_{19}H_{16}ONBr$, corresponding with I, but for the following reasons it seems certain that water has been lost from the *meso*-carbon atoms

and then taken up elsewhere in the molecule as water of crystallisation (II):

(i) The same amount of water is not present in all the salts.

(ii) It has been shown by Meisenheimer (*Annalen*, 1902, **323**, 205; 1904, **330**, 133), Guyot and Stähling (*Bull. Soc. chim.*, 1904, [iii], **33**, 1144), Clarke (*Ber.*, 1908, **41**, 935; *J. Amer. Chem. Soc.*, 1911, **33**, 1966) and other investigators that the *meso*-hydroxy-dihydroanthracene derivatives are very easily ethylated by boiling with alcoholic solutions of hydrogen chloride. Our salt, on the other hand, is not affected even by prolonged boiling with alcoholic solutions of hydrogen bromide.

(iii) If formula I were correct, the salt should behave towards primary aromatic amines in much the same way as 9 : 10-dihydro-anthraquinyldipyridinium dibromide. This, however, is not the case, as it is not affected even by boiling aniline.

Against the formula I it may be urged that as the "bridge" is intact the compound should be fluorescent, whereas neither the bromide nor any of the other salts which we have prepared shows any signs of visible fluorescence. Very little, however, is known as regards the influence of the pyridinium group on the fluorescence of organic compounds, and in any case the anhydrous salt, which must correspond with formula II, also exhibits no signs of fluorescence. The action of warm sodium hydroxide or other strongly alkaline solution on 9 : 10-dihydroanthraquinyldipyridinium dibromide leads to the replacement of one pyridinium group by the hydroxyl group and to the opening of the pyridine ring of the other group, the product being a monoanil of glutaconaldehyde, $C_{14}H_9N\colon CH\cdot CH\colon CH\cdot CH\colon CH\cdot OH$ or $C_{14}H_9NH\cdot CH\colon CH\cdot CH\colon CH\cdot CHO$.

The action of both primary and secondary aromatic amines on 9 : 10-dihydroanthraquinyldipyridinium dibromide leads to the displacement of both pyridinium groups, but only one substituted amino-group enters the molecule. The reaction is accompanied by simultaneous reduction, so that the products are derivatives of 9-amino-9 : 10-dihydroanthracene and have the general formula

$$C_6H_4{<}\begin{matrix}CH(NRAr)\\CH_2\end{matrix}{>}C_6H_4,$$

where Ar represents an aryl group and R an alkyl or aryl group or a hydrogen atom. The reaction seems to be a very general one, although in the case of β-naphthylamine there is a great tendency to form di-β-naphthylamine.

The reduction of the *meso*-carbon atoms of the anthracene ring system must be due to the production of glutaconaldehyde by the opening of one of the pyridine rings, and this view is supported by

the fact that ammonia is always present in the reaction products, and the smell of glutaconaldehyde can generally also be detected. Reduction is probably a secondary reaction, as the products are often extremely difficult to obtain pure and free from fluorescent admixtures. We have not as yet been able to establish the exact mechanism of the reaction, but as the action of the base causes an immediate liberation of pyridine it seems probable that the first step consists in the replacement of one pyridinium group by a substituted amino-group, the second pyridinium group being subsequently split off with rupture of the pyridine ring. The replacement of a pyridinium group by an arylamino-group has been observed by Zincke and Weisspfenning (*J. pr. Chem.*, 1910, [ii], **82**, 1), who obtained 3 : 5-dinitro-2-anilinobenzoic acid by boiling the pyridinium salt obtained from 2-chloro-3 : 5-dinitrobenzoic acid with aniline in glacial acetic acid solution. The reaction, however, is not a general one, and we have been unable to obtain any trace of phenylglycine by boiling the pyridinium salt derived from chloroacetic acid with aniline.

EXPERIMENTAL.

9 : 10-*Dihydroanthraquinyldipyridinium Dibromide.*

This salt can be obtained either by the direct union of pyridine with anthracene dibromide or, more conveniently, by the action of bromine on a suspension of anthracene in pyridine.

Anthracene (1·6 grams) was converted into the dibromide by treatment at 0° with 1·5 grams of bromine dissolved in 250 c.c. of carbon disulphide (Perkin, *Bull. Soc. chim.*, 1877, [ii], **27**, 464; *Chem. News*, 1876, **34**, 144). After about one and a half hours the dibromide was collected, washed with ice-cold ether, and suspended in 30 c.c. of pyridine. Formation of the pyridinium salt took place rapidly at the ordinary temperature; after three hours the white solid was collected, washed with ether, recrystallised from a mixture of alcohol and ether, and dried in a vacuum desiccator, when it formed a colourless, crystalline powder which melted at 166—167° (Found: C=57·7, 57·5; H=5·11, 4·91; N=5·77; Br=32·4. $C_{24}H_{20}N_2Br_2$ requires C=58·1; H=4·03; N=5·65; Br=32·2 per cent.).

In preparing the pyridinium salt by the direct action of bromine on anthracene in the presence of pyridine, it was found necessary to use sufficient bromine to convert the pyridinium bromide into the perbromide, as if this is not done a considerable amount of the anthracene is left unattacked. The following method was found to give extremely satisfactory results.

Technical refined anthracene (about 92 per cent.; 180 grams), suspended in 1800 c.c. of pyridine, is cooled to $-10°$ in a freezing mixture and bromine (480 grams) is run in very slowly, the whole being well agitated and the temperature being maintained below 0°. If the preparation is carried out in an enamelled iron vessel the addition of the bromine can be completed in about two and a half hours, but if a glass flask or beaker is used considerably more time is required owing to the less efficient cooling. When the bromine has been added the solution is set aside for an hour and the orange-yellow precipitate then collected with the aid of the pump and washed first with pyridine and then with ether. The yield is about 590 grams.

The perbromide is best reduced to the bromide by treatment with acetone. Scarcely any reduction takes place at the ordinary temperature, but on warming reduction takes place readily and the reaction may become violent, and on one occasion the acetone actually inflamed. For this reason it is best to add the perbromide little by little to boiling acetone. The reduction is easily followed by observing the change in colour from the yellow perbromide to the colourless bromide. When reduction is complete the precipitate is collected and washed with acetone. The resulting bromide is fairly pure, but can be purified by recrystallisation from a mixture of alcohol and ether (Found: C=58·1; H=4·6; N=5·64; Br=32·6, 32·5 per cent.).

9 : 10-*Dihydroanthraquinyldipyridinium dibromide* forms a colourless, crystalline powder, which is insoluble in ether, but moderately soluble in water or alcohol. When crystallised from warm water, it separates as a *hexahydrate*, but the water of crystallisation is lost very readily when the crystals are dried in a desiccator at the ordinary temperature (Found: C=47·9, 48·1; H=5·32, 5·93; N=5·04, 5·08; Br=26·9; H_2O=17·4, 17·5. $C_{24}H_{20}N_2Br_2,6H_2O$ requires C=47·7; H=5·3; N=4·6; Br=26·5; H_2O=17·9 per cent.).

When an aqueous solution of the salt is evaporated in a vacuum desiccator at the ordinary temperature, large, transparent needles separate, which appear to consist of a *pentahydrate* (Found: C=47·6; H=4·52; N=5·04; Br=27·7; H_2O=15·9. $C_{24}H_{20}N_2Br_2,5H_2O$ requires C=48·1; H=5·12; N=4·78; Br=27·3; H_2O=15·4 per cent.).

The *perbromide* is precipitated as an orange-red powder when bromine water is added to a cold aqueous solution of the bromide. It is insoluble in all the usual media, but appears to be identical in every way with the perbromide obtained by the action of bromine on anthracene in pyridine solution. The bromine was estimated by

Volhard's method after reduction with hydrazine sulphate (Found : Br=58·9. $C_{24}H_{20}N_2Br_6$ requires Br=58·8 per cent.). The *periodide* is precipitated as a violet powder when a solution of iodine in potassium iodide is added to an aqueous solution of the bromide. Owing to its insolubility in all media, we were unable to obtain it in a state of sufficient purity for analysis. It is not reduced by hydrazine.

The *hydrogen chromate* separates slowly in orange needles when a solution of potassium chromate is added to an aqueous solution of the bromide. It is almost insoluble in boiling water (Found: Cr=18·23. $C_{24}H_{20}N_2,2HCrO_4$ requires Cr=18·24 per cent.).

The *picrate* is precipitated when picric acid is added to an aqueous solution of the bromide. It melts at 168·5—170° and is almost insoluble even in boiling water (Found: N=14·4. $C_{36}H_{24}O_{14}N_8$ requires N=14·14 per cent.).

Preparation of Anthrone.

A solution of dihydroanthraquinyldipyridinium dibromide hexahydrate (50 grams) in 250 c.c. of water was heated on the water-bath in a current of carbon dioxide for four hours. The precipitated anthrone was then filtered off, washed with water, and dried in a vacuum desiccator. The yield was almost theoretical and the product was found to be free from anthraquinone and almost pure without further treatment (Found: C=86·3; H=5·33. Calc., C=86·6; H=5·15 per cent.).

Several attempts were made to combine the reduction of the perbromide and the removal of the pyridinium groups in one operation, but in every case the anthrone was contaminated with considerable quantities of anthraquinone and the yield was poor. On one occasion the perbromide was reduced with sulphurous acid, and the resulting solution boiled in a current of carbon dioxide. The small amount of anthrone which separated was filtered off, the filtrate neutralised with sodium hydroxide, and after removal of the sulphate and sulphite as barium salts concentrated somewhat and then cooled. The resulting crystals were collected, washed with water, and recrystallised several times from boiling water. They were found to be completely free from bromine and sulphur, and were identified as anthranylpyridinium chloride by the preparation of the picrate referred to below (Found: Cl=9·78, 9·84. $C_{19}H_{15}NCl,4H_2O$ requires Cl=9·74 per cent.).

On another occasion it was noticed that when the perbromide was suspended in water and treated with sulphurous acid in the cold it became decolorised without passing into solution. The colourless

substance contained nitrogen, bromine, and sulphur, and evolved sulphurous acid when warmed with water. Owing to its instability, it was not possible to obtain it in a state of purity, but it is probably a sulphurous ester of 9-hydroxy-9 : 10-dihydroanthracene-10-pyridinium bromide, for as has already been pointed out, hydroxyl groups attached to the *meso*-carbon atoms of the anthracene complex are very easily esterified.

Action of Sodium Hydroxide on 9 : 10-*Dihydroanthraquinyl-dipyridinium Dibromide.*

To 35 grams of dihydroanthraquinyldipyridinium dibromide hexahydrate dissolved in 500 c.c. of water and cooled to 15°, 100 c.c. of *N*/2-sodium hydroxide were added. Crystals commenced to form in about ten minutes and separation was complete after an hour. The solution was cooled to 0°, the precipitate collected, washed with a little ice-water and crystallised from boiling water. The yield was 14 grams (Found: C=64·2; H=5·15; N=3·89; Br=22·3. $C_{19}H_{14}NBr,H_2O$ requires C=64·4; H=4·52; N=3·96; Br=22·6 per cent.).

Anthranylpyridinium bromide forms lemon-yellow leaflets or needles insoluble in ether, but moderately easily soluble in water or alcohol. It loses water of crystallisation slowly at 110°, but more rapidly at 150° (Found: H_2O=4·95. $C_{19}H_{14}NBr,H_2O$ requires H_2O=5·09 per cent.). Addition of bromine water to its aqueous solution causes immediate precipitation of the *perbromide* as an oil, which soon becomes solid and can then be recrystallised from boiling methyl alcohol, from which it separates in orange-red needles almost insoluble in water. The bromine was estimated by Volhard's method after reduction with hydrazine (Found: Br=46·1. $C_{19}H_{16}ONBr_3$ requires Br=46·7 per cent.).

The *dichromate* is precipitated by adding potassium dichromate to an aqueous solution of the bromide. It crystallises from boiling water, in which it is very sparingly soluble, in orange-red needles (Found: Cr=14·38. $[C_{19}H_{14}N]_2Cr_2O_7$ requires Cr=14·29 per cent.).

The *picrate* is precipitated from an aqueous solution of the bromide by the addition of picric acid. It crystallises from boiling water, in which it is very sparingly soluble, in yellow needles which melt at 180—182° (Found: C=61·1; H=4·52; N=11·59. $C_{25}H_{16}O_7N_4,\frac{1}{2}H_2O$ requires C=60·9; H=3·45; N=11·35 per cent.). A picrate prepared from the bromide which had been dehydrated by heating at 150° also melted at 180—182° and the melting point was not changed by admixture of the picrate made from the hydrated bromide.

When dihydroanthraquinyldipyridinium dibromide is treated with warm sodium hydroxide solution (2 mols.), not only is one pyridinium group displaced, but the pyridine ring of the remaining group is ruptured. The resulting product, however, is rather difficult to purify owing to its tendency to become resinous. The following procedure, however, seemed to give a pure product. To dihydroanthraquinyldipyridinium dibromide (15 grams) dissolved in 200 c.c. of water at 50° were added 100 c.c. of $N/2$-sodium hydroxide. The temperature was then slowly raised to 70° and maintained at this point for half an hour. After dilution with a large volume of cold water, the red precipitate was collected, washed with cold water, dried in a vacuum desiccator, dissolved in chloroform, and reprecipitated from the filtered solution by the addition of ether. The yield was only 0·3 gram (Found: C=80·7; H=5·46. $C_{19}H_{15}ON,\frac{1}{2}H_2O$ requires C=80·8; H=5·67 per cent.). The substance forms a chocolate-brown powder which is easily soluble in chloroform, but less soluble in alcohol, benzene or light petroleum.

Action of Ammonia and Primary and Secondary Aliphatic Amines.

Dihydroanthraquinyldipyridinium dibromide in quantities of 15 grams ($\frac{1}{30}$-gram-mol.) was dissolved in 200 c.c. of water and the solutions were cooled to 10° and treated with exactly one equivalent of a 10 per cent. solution of ammonia, monomethylamine, dimethylamine,* and piperidine. In all cases the separation of crystals commenced in a few minutes and was allowed to proceed for one and a half hours, when the solutions were cooled to 0° and the precipitate was collected, washed with a little ice-water, and recrystallised from boiling water or a mixture of alcohol and ether. All the products were characterised as being identical with the anthranylpyridinium bromide obtained by the action of sodium hydroxide, the identification being effected both by analysis and by the preparation of the picrate and the determination of its melting point alone and when mixed with the picrate made from the salt obtained by the action of sodium hydroxide (Found: C=64·2, 64·2, 64·1, 64·3; H=4·41, 4·47, 4·97, 4·20; N=4·08, 4·10; Br=22·4, 22·3, 22·4. Calc., C=64·4; H=4·52; N=3·96; Br=22·6 per cent.). The yields obtained in all cases were about 6 grams.

Action of Pyridine and Quinoline.

An aqueous solution of dihydroanthraquinyldipyridinium dibromide was gently warmed on the water-bath with one gram-

* Kindly supplied by British Dyestuffs Corporation, Ltd.

equivalent of pyridine or quinoline. At the end of an hour the solution was treated with picric acid and the resulting precipitate collected, washed with hot water, and recrystallised from boiling water. In both cases the product melted at 180—182°, and no change in melting point was observed after admixture of anthranylpyridinium picrate prepared from dihydroanthraquinyldipyridinium dibromide by means of sodium hydroxide.

Action of Primary and Secondary Aromatic Amines.

The conversion of dihydroanthraquinyldipyridinium dibromide into derivatives of 9-amino-9 : 10-dihydroanthracene by the action of primary and secondary aromatic amines can be carried out by heating the salt with the amine either without a solvent or in the presence of alcohol; which method gives the best results depends on the particular amine that is being used.

In some cases the reaction takes place smoothly and the aminodihydroanthracene derivative is easily obtained pure and in fair yield. In other cases, however, the yields are very poor and the product only obtained pure after repeated crystallisation.

9-*Phenylamino*-9 : 10-*dihydroanthracene*.—This substance is very easily obtained when dihydroanthraquinyldipyridinium dibromide is boiled for a few minutes with excess of aniline, with or without the addition of alcohol. When the whole of the pyridinium salt has dissolved, the solution is cooled, poured into dilute hydrochloric acid, and the precipitate collected and washed with dilute hydrochloric acid. The substance is usually obtained pure after a single recrystallisation from alcohol (Found: C=88·5; H=6·22; N=5·01. M [in naphthalene solution] =262. $C_{20}H_{17}N$ requires C=88·5; H=6·27; N=5·16 per cent. M=271). It crystallises in yellow leaflets which melt at 197—200°.

9-o-*Nitrophenylamino*-9 : 10-*dihydroanthracene*.—Five grams of dihydroanthraquinyldipyridinium dibromide were boiled under reflux with 3 grams of *o*-nitroaniline and 50 c.c. of alcohol. The pyridinium salt was completely dissolved at the end of an hour, but boiling was continued for another half-hour. After cooling, the solution was poured into dilute hydrochloric acid and the very viscous precipitate separated as far as possible from the liquors and washed with dilute hydrochloric acid. It was purified by recrystallisation twice from a mixture of alcohol, acetone, and water, and then formed glistening, brick-red needles which melted at 219—220°. The yield was 0·5 gram (Found: C=76·2; H=5·05. $C_{20}H_{16}O_2N_2$ requires C=75·9; H=5·05 per cent.).

9-m-*Nitrophenylamino*-9 : 10-*dihydroanthracene* was made in the

same way as the *o*-nitro-compound, but the precipitate obtained on pouring the alcoholic solution into dilute hydrochloric acid was much less viscous. It was obtained pure after a single recrystallisation from a mixture of acetone, alcohol, and water, and then formed bright red needles which melted at 199—200°. The yield was 1·2 grams (Found: C=75·8; H=5·01; N=8·89. $C_{20}H_{16}O_2N_2$ requires C=75·9; H=5·05; N=8·86 per cent.).

9-p-*Nitrophenylamino*-9 : 10-*dihydroanthracene* was made in the same way as the o- and *m*-nitro-compounds, but the precipitate obtained by pouring the alcoholic solution into dilute hydrochloric acid was very viscous, although it became solid on keeping. The product was purified by recrystallising three times from a mixture of methyl ethyl ketone, alcohol, and water, and then twice from absolute alcohol. It was then obtained in the form of microscopic lemon-yellow needles, which melted at 179—180°. The yield was 0·4 gram (Found: C=76·0; H=5·15; N=8·56. $C_{20}H_{16}O_2N$ requires C=75·9; H=5·05; N=8·86 per cent.).

9-o-*Tolylamino*-9 : 10-*dihydroanthracene*.—Ten grams of dihydro anthraquinyldipyridinium dibromide were heated at 150° for an hou with 20 grams of *o*-toluidine, and the whole was then poured int dilute hydrochloric acid and boiled. The resulting precipitate wa collected, washed first with dilute hydrochloric acid and then wit water, and recrystallised six times from a mixture of methyl eth ketone and alcohol, when it was obtained in lemon-yellow needl which melted at 158—160° (Found: C=88·7; H=6·67. $C_{21}H_{19}$ requires C=88·4; H=6·63 per cent.).

9-p-*Tolylamino*-9 : 10-*dihydroanthracene* was prepared in the san way as the *o-toluidino-compound* and was purified by recrystalli ing four times from a mixture of methyl ethyl ketone and alcoh and then twice from absolute alcohol. The yield of pure produ obtained from 10 grams of the dipyridinium dibromide was 0·7 gra It formed minute, yellow needles which melted at 160—16 (Found: C=88·4; H=6·50. $C_{21}H_{19}N$ requires C=88·4; H=6· per cent.).

9-o-*Carboxyphenylamino*-9 : 10-*dihydroanthracene*.—Ten grams dihydroanthraquinyldipyridinium dibromide were boiled un reflux with 5 grams of anthranilic acid and 75 c.c. of alcohol three hours, and the whole was then cooled and poured slowly i a large volume of cold water. The extremely viscous precipit which formed was separated as far as possible from the moth liquors and dissolved in 500 c.c. of boiling methyl ethyl ketc The greater part of the solvent was removed by distillation on water-bath and the solution filtered and cooled in ice. The result crystals were collected, washed with methyl ethyl ketone, and

solved in 300 c.c. of the same solvent. After concentration to a small volume, the solution was cooled in ice and then deposited glistening, lemon-yellow crystals which decomposed at 255—275° when heated. The yield was 1·1 grams (Found: C=80·2; H=5·08. $C_{21}H_{17}O_2N$ requires C=80·0; H=5·40 per cent.).

9-p-*Benzeneazophenylamino*-9 : 10-*dihydroanthracene*.—Five grams of dihydroanthraquinyldipyridinium dibromide and 4 grams of *p*-aminoazobenzene were boiled under reflux with 50 c.c. of alcohol for one and a half hours. After cooling, the whole was poured into dilute hydrochloric acid and the precipitate collected and washed repeatedly with large volumes of boiling dilute hydrochloric acid. It was purified by recrystallising first from aqueous acetone and then from a mixture of acetone and alcohol, and formed yellowish-brown needles which melted at 230·5—231·5°. The yield was 1·1 grams (Found: N=11·19. $C_{26}H_{21}N_3$ requires N=11·20 per cent.).

9-β-*Naphthylamino*-9 : 10-*dihydroanthracene*.—Twenty grams of dihydroanthraquinyldipyridinium dibromide and 12 grams of β-naphthylamine were boiled under reflux for three hours with 200 c.c. of alcohol and the solution was then cooled and poured into a large bulk of dilute hydrochloric acid. The resulting flocculent precipitate was collected and repeatedly ground with large quantities of slightly warm, very dilute hydrochloric acid. It was finally dried in a vacuum desiccator and then repeatedly crystallised, first from a mixture of benzene and light petroleum and then from alcohol containing a little acetone. The yield was about 0·5 gram, and the product melted indefinitely at 182—207° (Found: C=91·1; H=5·85. $C_{24}H_{19}N$ requires C=89·7; H=5·92 per cent.).

When dihydroanthraquinyldipyridinium dibromide is heated for a short time at 150—180° with twice its weight of β-naphthylamine the chief product is di-β-naphthylamine. This can be obtained in the pure state by pouring the hot melt into a large volume of boiling dilute hydrochloric acid and washing the precipitate repeatedly with boiling water in order to remove the excess of β-naphthylamine. The crude product is best purified by repeated recrystallisation, first from aqueous pyridine and then from methyl ethyl ketone. The identification was effected by analysis and by the method of mixed melting points both of the free base and of the picrate (Found: C=89·0; H=5·99. Calc., C=89·2; H=5·58 per cent.).

It is remarkable that there is no difficulty in obtaining a crude product the melting point of which (170—171°) is not changed by admixture with di-β-naphthylamine, but analysis shows that a pure product is only obtained after repeated recrystallisation. The

impure substance also gives a picrate which melts at 165—167° and shows no change in melting point when mixed with di-β-naphthylamine picrate.

Several attempts were made to prepare the corresponding α-naphthylaminodihydroanthracene, but owing to its refusal to crystallise it was not found possible to isolate it in the pure state.

9-Phenylmethylamino-9 : 10-dihydroanthracene.—Thirty grams of dihydroanthraquinyldipyridinium dibromide and 30 grams of monomethylaniline were heated at 150—160° until a clear solution was obtained. The whole was then poured into concentrated hydrochloric acid and the solution diluted with its own volume of water and boiled. The precipitate was collected, washed successively with boiling dilute hydrochloric acid and boiling water, and crystallised first from aqueous pyridine and then repeatedly from a mixture of methyl ethyl ketone and alcohol, when it formed yellow needles which melted at 141·5—143·5°. The yield was about 1·5 grams (Found: C=88·3; H=6·70. M [in naphthalene solution] =268. $C_{21}H_{19}N$ requires C=88·4; H=6·70 per cent. M=285).

Similar compounds can be obtained from monoethylaniline and from benzylaniline, but it was not found possible to obtain them pure. It is perhaps worth mentioning that a sample of the benzylaniline derivative which had been crystallised repeatedly, first from light petroleum and then from a mixture of alcohol and acetone, was found to exhibit remarkable electrical properties and to become strongly luminous when rubbed with a horn spatulum. The sample in question melted at 137—138° and formed yellow needles. Its solutions exhibited a very powerful greenish-blue fluorescence.

9-Diphenylamino-9 : 10-dihydroanthracene.—Thirty grams of dihydroanthraquinyldipyridinium dibromide and 25 grams of diphenylamine were heated during about twelve hours on the water-bath with frequent agitation until a sample no longer gave a red precipitate when boiled with dilute sodium hydroxide solution; absolute alcohol (50 c.c.) was then added and the whole boiled. After cooling, the precipitate was collected and washed with absolute alcohol. The purification of the product was found to be somewhat troublesome, but experience showed that it was best effected by repeated crystallisation first from a mixture of methyl ethyl ketone and alcohol, then from aqueous pyridine, and finally again from a mixture of methyl ethyl ketone and alcohol. The purified product formed greenish-yellow leaflets and melted at 226—227·5° (Found: C=90·2; H=6·27. $C_{26}H_{21}N$ requires C=89·9; H=6·05 per cent.).

In conclusion, the authors desire to express their thanks to the British Alizarine Co., Ltd., the South Metropolitan Gas Co., Ltd.,

and the Gas, Light and Coke Co., Ltd., for the supply of anthracene and pyridine, and to the Research Grant Committee of the Chemical Society for a grant which has partly defrayed the expenses of this research.

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CII.—*Organo-derivatives of Bismuth. Part IV. The Interaction of the Halogen derivatives of Tertiary Aromatic Bismuthines with Organo-derivatives of Magnesium and Mercury.*

By FREDERICK CHALLENGER and CHARLES FREDERICK ALLPRESS.

IN consequence of the failures which accompanied many attempts to prepare mixed aromatic bismuthines of the type $BiR'R_2''$ and bismuthonium haloids $BiR_3'R''X$, the action of the Grignard reagent on halogen derivatives of the types BiR_2X, $BiRX_2$, and BiR_3X_2 has been carefully studied. For this purpose several new halogen derivatives have been prepared. Bismuth chloride (1 mol.) and tri-*p*-tolylbismuthine (2 mols.) yield chiefly *di*-p-*tolylchlorobismuthine*, m. p. 181°, a small amount of p-*tolyldichlorobismuthine*, m. p. 207°, being also produced, as frequently happens in reactions of this type. *Di-α-naphthylchlorobismuthine*, m. p. 168°, is similarly formed, although with some difficulty, from bismuth chloride and tri-α-naphthylbismuthine. In whatever proportion this bismuthine and bismuth bromide are mixed, however, the product is α-naphthyldibromobismuthine, m. p. 208°. This is also produced together with α-bromonaphthalene and tri-α-naphthylbismuthine when tri-α-naphthylbismuthine dibromide is heated at 100°. The production of the dibromobismuthine seems of interest, since in boiling benzene triphenylbismuthine dichloride and dibromide yield diphenylchlorobismuthine and the corresponding bromo-compound.

α-Naphthyldibromobismuthine is also formed when iodine bromide (1 mol.) and tri-α-naphthylbismuthine interact, some bismuthine remaining unchanged. In these cases a special tendency appears to exist for the formation of the dibromo- in preference to the monobromo-derivative.

Phenyldibromobismuthine (T., 1914, **105**, 2215; 1916, **109**, 250)

is the main product obtained from two mols. of bismuth bromide and one mol. of triphenylbismuthine.

Tri-m-*tolylbismuthine*, m. p. 65°, has been prepared from bismuth chloride and magnesium *m*-tolyl bromide.

The use of sulphuryl chloride in chloroform solution at the ordinary temperature (T., 1916, **109**, 251) appears to be a general method for the preparation of bismuthine dichlorides; traces of organic sulphur compounds are, however, simultaneously produced. The dichlorides of tri-*p*-tolyl- and tri-α-naphthyl-bismuthines have been prepared in this manner.

With the magnesium derivative of *p*-iodo-*m*-xylene, diphenylchlorobismuthine and di-*p*-tolylchlorobismuthine gave triphenyl- and tri-*p*-tolyl-bismuthines respectively. Magnesium phenyl bromide (1 or 2 mols., as required by theory) gave with di-α-naphthylchlorobismuthine and α-naphthyldibromobismuthine the tri-α-naphthylbismuthine and in the latter instance a trace of diphenyl-α-naphthylbismuthine. With 1·2 mols. of magnesium α-naphthyl bromide, di-*p*-tolylchlorobismuthine similarly gave tri-*p*-tolylbismuthine. In most of these experiments a certain amount of bismuth oxide or oxyhaloid was produced on addition of water.

The constant production in these reactions of the bismuthine from which the original halogen compound was derived would appear to indicate that BiR_2X or $BiRX_2$ might react as a mixture of BiR_3 and BiX_3, but then the simultaneous production of a tertiary bismuthine containing only the radicle of the Grignard reagent would be expected.

Except in the aliphatic series, where the odour of an alkylbismuthine was detected (T., 1914, **105**, 2216; 1916, **109**, 250). and in cases where large excess of the Grignard reagent was employed, this has not been observed. It appeared possible that in the absence of a large excess of the Grignard solution * much of the halogen bismuthine might remain unattacked,† although in almost every instance it completely dissolved. On decomposition with water, reaction with the magnesia might then occur thus:

$$6BiPh_2Br + 3Mg(OH)_2 = 4BiPh_3 + 2Bi(OH)_3 + 3MgBr_2.$$

This type of reaction has been shown to occur with phenyl- and α-naphthyl-dibromobismuthines and diphenylbromobismuthine in

* Compare the necessity for such excess in the preparation of the tetra-derivatives of tin and lead (Grüttner and Krause, *Ber.*, 1919, **52**, [*B*], 2159; Krause and Becker, *ibid.*, 1920, **53**, [*B*], 17) and the organo-derivatives of mercury (Hilpert and Grüttner, *Ber.*, 1915, **48**, 906).

† This appears to be the case, *for example*, when 2½ *mols. of* magnesium α-naphthyl bromide interact with phenyldibromobismuthine. See also p. 922.

presence of aqueous ammonia, sodium hydroxide, or magnesium oxide. With water or alcohol alone, however, only hydrocarbon and bismuth oxyhaloid are produced. (An account of these and other properties of the halogen derivatives of the bismuthines will shortly be communicated to the Society in conjunction with Mr. J. F. Wilkinson.)

This hypothesis, although probably correct in some cases, does not explain the production of triphenylbismuthine from diphenylbromobismuthine and magnesium α-naphthyl bromide or magnesium ethyl bromide when the reaction mixture is worked up in the absence of water.

The complex nature of some of the changes involved is shown by the production of triphenylbismuthine and diphenyl-α-naphthylbismuthine by the action of six molecules of magnesium phenyl bromide on α-naphthyldibromobismuthine. The interchange of groups observed when mercury diphenyl is employed (p. 923) may be analogous. Similarly, with 5½ mols. of magnesium α-naphthyl bromide, phenyldibromobismuthine gives rise to much tri-α-naphthylbismuthine.

The action of magnesium phenyl bromide and magnesium methyl iodide on tri-α-naphthylbismuthine dibromide yields tri-α-naphthylbismuthine, in the second case, without the addition of water. In the first case the reaction proceeds thus :

$$(C_{10}H_7)_3BiBr_2+MgPhBr=(C_{10}H_7)_3Bi+PhBr+MgBr_2.$$

Diphenyl does not appear to be formed in quantity much greater than that already present in the Grignard solution.

It was of interest to determine whether this reducing action of the Grignard reagent,* which is so frequently noticed in connexion with the dihaloids of the tellurides (Lederer, *Ber.*, 1916, **49**, 1615; 1920, **53**, [*B*], 713, 1674) and bismuthines, is also exerted on the corresponding arsenic and antimony compounds. We find that triphenylarsine is produced from its dichloride and magnesium phenyl bromide or magnesium methyl iodide. Triphenylstibine dichloride is reduced to the stibine when treated with magnesium methyl iodide, possibly by way of $SbPh_3I_2$, since iodobenzene is also produced.

The yield of triphenylbismuthine from mercury diphenyl and bismuth bromide is nearly quantitative and better than that obtained with the Grignard reagent (60 per cent.). The reaction

* The metal or a lower haloid is also produced by the action of the Grignard reagent on salts of lead, copper, mercury(ous), thallium and chromium, whilst Hepworth (T., 1921, **119**, 253) has shown that nitric esters similarly give rise to traces of dialkylamines.

of mercury diphenyl with α-naphthyldibromobismuthine is, however, most unexpected, mercury phenyl bromide, triphenylbismuthine, and mercury di-α-naphthyl being obtained. This recalls the ease with which mercury phenyl bromide yields mercury diethyl and mercury dibenzyl with the appropriate Grignard reagent (Hilpert and Grüttner, *loc. cit.*).

In marked distinction to the behaviour of α-naphthyldibromobismuthine, tri-α-naphthylbismuthine dibromide does not react with mercury diphenyl at room temperature. In boiling benzene, however, a somewhat complicated reaction occurs analogous with that of magnesium phenyl bromide, tri-α-naphthylbismuthine, mercury phenyl bromide, and bromobenzene being obtained, as also triphenylbismuthine and mercury di-α-naphthyl in much smaller quantities. The last two compounds probably arise from the action of mercury diphenyl on traces of α-naphthylbromobismuthines arising from the decomposition of the dibromide (see p. 919). In agreement with this is the fact that only traces of α-bromonaphthalene seem to be produced. Preliminary experiments have been made on the interaction of the aromatic bismuthines with the salts of other metals. With alcoholic silver nitrate, fine yellow or orange-yellow, crystalline precipitates are produced, which are probably similar to or identical with the $AgNO_3,2AgC_6H_5$ described by Krause and Schmitz (*Ber.*, 1919, **52**, [*B*], 2150).

As these authors desire to continue the investigation of these products, we do not propose further to examine the silver compounds we have obtained. It appears, however, that in this case triphenylbismuthine can act as a phenylating agent, as has already been observed with mercuric chloride (Gillmeister, *Ber.*, 1897, **30**, 2844). Other reactions of this type are being investigated in conjunction with Mr. L. R. Ridgway.

Bismuth chloride combines with benzenediazonium chloride to form a stable, well-crystallised additive product. Its behaviour with sodium hydroxide and similar reagents is under examination with a view to the possible production of the bismuth analogues of the arsinic and stibinic acids.

EXPERIMENTAL.

Action of Iodine Monochloride on Diphenyl-α-naphthylbismuthine.

Diphenyl-α-naphthylbismuthine (0·8 gram) was treated with 0·26 gram of iodine monochloride, both in chloroform–ether solution. A brown turbidity was produced, which disappeared on shaking, and, on standing, a colourless solid separated. On crystallisation

from chloroform–ether, this melted at 182° (diphenylchlorobismuthine melts at 184—185°).

The mother-liquor and washings were evaporated, separated from a further small deposit with light petroleum, glacial acetic acid was added and the cooled solution treated with chlorine, when 0·15 gram of α-iodonaphthalene dichloride was obtained.

Action of Cyanogen Iodide on Tri-α-naphthylbismuthine.

Three grams of tri-α-naphthylbismuthine and 0·76 gram (1 mol.) of cyanogen iodide were boiled in 30 c.c. of dry chloroform for four hours. On adding ether, 1·2 grams of unchanged bismuthine were recovered. The mother-liquors, still smelling of cyanogen iodide, gave a brownish-yellow deposit, which on extraction with light petroleum and treatment with chlorine gave a very small quantity (less than 0·05 gram) of α-iodonaphthalene dichloride. The reaction occurs less readily than with triphenylbismuthine.

*Di-*p*-tolylchlorobismuthine and* p*-Tolyldichlorobismuthine.*

On mixing dry ethereal solutions of bismuth chloride and tri-*p*-tolylbismuthine, a turbidity was produced, and crystals gradually deposited. These were separated, washed with ether, dried, and recrystallised from chloroform–ether (free from alcohol and specially dried), leaving a yellow substance (m. p. 207°) almost insoluble in chloroform. After four crystallisations, the main bulk melted constantly at 180°, and no further yellow product was obtained (Found: Cl=8·43; Bi=49·16. $C_{14}H_{14}ClBi$ requires Cl=8·34; Bi=48·89 per cent.).

*Di-*p*-tolylchlorobismuthine* forms colourless needles, m. p. 181°, moderately soluble in hot benzene and chloroform, and almost insoluble in ether and light petroleum.

The yellow substance was crystallised from dry benzene (Found: Cl=18·80. $C_7H_7Cl_2Bi$ requires Cl=19·19 per cent.). p-*Tolyldichlorobismuthine* forms yellow needles, m. p. 206—207°, difficultly soluble in hot benzene and almost insoluble in other solvents.

Both these compounds are decomposed by alcohol and moist solvents, and with hydrochloric acid give toluene and bismuth chloride.

Action of Sodium on Diphenylbromobismuthine and α-Bromonaphthalene.

Diphenylbromobismuthine (m. p. 157°) (6·63 grams), α-bromonaphthalene (3·1 grams) and sodium (0·35 gram) were heated with

benzene for about twenty hours, filtered hot, and the solvent evaporated. The residue solidified on cooling (m. p. 74—76°), and, on recrystallisation from alcohol, was shown to consist of triphenylbismuthine.

When diphenylchlorobismuthine, α-bromonaphthalene and sodium were heated in benzene, triphenylbismuthine was produced, as also a greyish-black solid insoluble in benzene, which contained bismuth but no organic matter, some of the bismuth being probably present as the metal (Challenger, T., 1916, **109**, 250). The method appears quite unsuitable for the preparation of a mixed bismuthine.

Action of Copper Bronze on Phenyldibromobismuthine.

A small quantity of phenyldibromobismuthine was boiled with dry benzene and copper bronze for three hours, the reaction commencing at the ordinary temperature. The black solution on concentration and treatment with alcohol deposited triphenylbismuthine, which after one crystallisation melted at 79°. The black colour was due to metallic bismuth, which was isolated from the residue, and not to the presence of organic compounds containing a high percentage of bismuth, analogous to the arsenic derivatives described by Fargher (T., 1920, **117**, 865) or by Ehrlich and Karrer (*Ber.*, 1913, **46**, 3564). Linkage of the bismuth atoms appears not to occur.

Di-α-naphthylchlorobismuthine.

Tri-α-naphthylbismuthine (3·54 grams) in the minimum quantity of cold dry chloroform (free from alcohol), was treated with 0·96 gram of bismuth chloride in ether–chloroform solution. After standing a few minutes, some bismuth oxychloride was precipitated and filtered off. The solution, on addition of more ether, gradually deposited a grey powder and a flocculent mass of yellow needles. These, after one crystallisation from chloroform–ether, had a constant melting point of 168°. The mother-liquor from the original deposit yielded bismuth chloride and naphthalene (Found Bi=41·34; Cl=7·56. $C_{20}H_{14}ClBi$ requires Bi=41·81; Cl=7·14 per cent.).

Other preparations similarly gave deposits of bismuth oxychloride, although every care was taken to have absolutely dry flasks and solvents, and in two cases unchanged tri-α-naphthylbismuthine and bismuth chloride were isolated, showing the comparative difficulty with which the reaction occurs.

Di-α-naphthylchlorobismuthine forms fine, yellow needles, moder-

ately soluble in dry benzene and chloroform, much less so in ether and light petroleum. It is extremely susceptible to traces of moisture, and even after keeping a short time in a closed vessel loses its yellow colour, and smells of naphthalene.*

α-Naphthyldibromobismuthine.

Bismuth bromide (1·5 grams; 1 mol.) in dry ether was added to 3·9 grams (2 mols.) of tri-α-naphthylbismuthine in dry chloroform. After keeping, the mother-liquor was poured off, and the orange-coloured solid washed with ether. On crystallisation from benzene it melted at 208° (Found: Br=32·74. $C_{10}H_7Br_2Bi$ requires Br=32·32 per cent.).

The mother-liquor, on concentration, gave 1·95 grams of unchanged tri-α-naphthylbismuthine, further proof of the non-formation of di-α-naphthylbromobismuthine.

Tri-α-naphthylbismuthine (2·95 grams; 1 mol.) in chloroform and 4·1 grams of bismuth bromide (2 mols.) in ether gave a deep orange, crystalline deposit, which was recrystallised from benzene (Found: Br=32·44; Bi=41·06. $C_{10}H_7Br_2Bi$ requires Br=32·32; Bi=42·00 per cent.).

α-Naphthyldibromobismuthine is a deep orange, crystalline solid melting and decomposing at 208°. It is difficultly soluble in benzene and almost insoluble in other solvents.

Formation of α-Naphthyldibromobismuthine from Tri-α-naphthylbismuthine Dibromide.

A quantity of dry tri-α-naphthylbismuthine dibromide was heated for half an hour at 100° in the absence of moisture, when it melted in the course of a few minutes. The pasty mass, after being washed with dry ether to remove α-bromonaphthalene, was extracted with chloroform-ether, yielding tri-α-naphthylbismuthine, m. p. 230°. The residue was extracted with benzene, giving orange crystals, melting at 208°, and consisting of α-naphthyldibromobismuthine. The final residue was bismuth oxybromide.

Preparation of Phenyldibromobismuthine.

On adding 1·5 grams of triphenylbismuthine in ethereal solution to 3·0 grams of bismuth bromide in the same solvent, yellow crystals, m. p. 201°, were deposited, which on recrystallisation from dry

* Phenyldichlorostibine and phenyldi-iodostibine also decompose on keeping (Schmidt, *Annalen*, 1920, **421**, 219).

benzene melted at 202° (T., 1914, **105**, 2216) (Found: Br=36·33. $C_6H_5Br_2Bi$ requires Br=35·93 per cent.).

*Tri-*m*-tolylbismuthine.*

Bismuth chloride (23 grams) in ether was slowly added with frequent shaking to a solution prepared from magnesium (6 grams; 3·3 atoms) and *m*-bromotoluene (39 grams; 3 mols.) in dry ether. On the next day the solvent was removed, ice added, toluene removed in steam, and the filtered residue extracted with acetone. The solution deposited 9 grams of white needles, m. p. 56°, mixed with some oil which soon solidified. On crystallisation from acetone and finally from alcohol, these melted at 65° (Found: Bi=43·40, 43·35. $C_{21}H_{21}Bi$ requires Bi=43·25 per cent.).

*Action of Magnesium α-Naphthyl Bromide on Di-*p*-tolylchlorobismuthine and of Magnesium Phenyl Bromide on Di-α-naphthylchlorobismuthine.*

(*a*) Di-*p*-tolylchlorobismuthine (1·7 grams) and the Grignard reagent (1·2 mols.) gave only tri-*p*-tolylbismuthine.

(*b*) Di-α-naphthylchlorobismuthine (2·5 grams) and the Grignard reagent gave 1·6 grams of tri-α-naphthylbismuthine.

In (*a*) the Grignard reagent was added to the halogen bismuthine, in (*b*) the reverse method was adopted, with no apparent reaction at the ordinary temperature in either case. After five hours on the water-bath the reaction seemed complete in (*a*) and almost so in (*b*). The ether was evaporated, water added, and the filtered residues extracted with in (*a*) alcohol and (*b*) chloroform. The products obtained from these extracts did not depress the melting points of the respective bismuthines.

*Action of the Magnesium Derivative of *p*-Iodo-*m*-xylene on Diphenylchlorobismuthine and Di-*p*-tolylchlorobismuthine.*

(*a*) Diphenylchlorobismuthine (4 grams), magnesium (0·3 gram) and iodoxylene (2·8 grams) gave triphenylbismuthine.

(*b*) Di-*p*-tolylchlorobismuthine (11 grams), magnesium (0·7 gram), and iodoxylene (7·1 grams) gave tri-*p*-tolylbismuthine.

The Grignard reagent was added to the halogen bismuthine. After three hours on the water-bath in (*a*) and twelve hours at room temperature in (*b*), the ether was removed, water added and the filtered residue containing much bismuth oxyhaloid (seeming from unchanged halogen bismuthine) extracted with benzene-alcohol.

Action of Magnesium Phenyl Bromide and Magnesium p-*Tolyl Bromide on α-Naphthyldibromobismuthine.*

(I) The dibromobismuthine (13 grams; 1 mol.) was added to 2·5 mols. of magnesium phenyl bromide (1·59 grams of magnesium; 10·3 grams of bromobenzene). A vigorous reaction took place. The solid immediately disappeared and was gradually replaced by a yellow oil. The ether was evaporated, the residue decomposed by water, filtered, and extracted with benzene. Alcohol was added to the solution so obtained, giving a yellow oil, which slowly became semi-solid, and on washing with light petroleum gave crystals, m. p. 212—220° (1·3 grams). After three recrystallisations, these melted at 232°, and did not depress the melting point of tri-α-naphthylbismuthine. The alcohol–benzene solution deposited traces of an oily solid, which on washing with light petroleum and recrystallising from alcohol melted at 115—116°, and did not depress the m. p. of diphenyl-α-naphthylbismuthine.

(II) When a mixture of 25 grams of α-naphthyldibromobismuthine (free from bismuth bromide) with magnesium phenyl bromide (6 mols.) was kept at room temperature for two weeks, the ether removed, and the residue, without further heating, distilled in steam, more satisfactory results were obtained. Extraction with acetone and alternate crystallisation from chloroform–alcohol and aqueous alcohol gave triphenylbismuthine and diphenyl-α-naphthylbismuthine in almost equal amounts, about 4 grams. No tri-α-naphthylbismuthine or phenyldinaphthylbismuthine was isolated in this case. This seems to be the best method for preparing the mixed bismuthine. When the mixture was heated instead of remaining at room temperature, the yield of this product was much smaller.

(III) α-Naphthyldibromobismuthine (4 grams) and magnesium *p*-tolyl bromide (about 3·5 mols.) were heated during four hours on the water-bath. The decanted ether yielded crystals, m. p. 222°, which on recrystallisation melted at 234—235°, and did not depress the m. p. of tri-α-naphthylbismuthine. A further quantity was obtained from the insoluble residue.

Action of Magnesium α-Naphthyl Bromide on Diphenylbromobismuthine.

Diphenylbromobismuthine (10 grams) and the Grignard reagent * (1·2 mols.) were heated under reflux for some hours, the ether

* Concentrated solutions of magnesium α-naphthyl bromide on keeping frequently deposit magnificent crystals, presumably of the etherate. These redissolve on warming.

was decanted, and without addition of water the residue extracted with light petroleum and then with chloroform. From these solutions triphenylbismuthine, bismuth oxybromide, and some unchanged diphenylbromobismuthine were obtained. The mixed bismuthine was probably present, but in this case was not isolated from the viscous mass.

Action of Magnesium Ethyl Bromide on Diphenylbromobismuthine.

This was carried out as previously (T., 1914, **105**, 2216), but after removal of the ether the residue was extracted with light petroleum without addition of water. Triphenylbismuthine and the odour of an alkylbismuthine were produced and the extract deposited a yellow powder, which took fire explosively on heating in air, and was probably an oxidation product of triethylbismuthine.

Action of Magnesium Phenyl Bromide on Tri-α-naphthylbismuthine Dibromide.

(I) The dibromide (23 grams) was treated with the Grignard reagent (2 mols.; 9·5 grams of bromobenzene, 1·5 grams of magnesium, and 70 c.c. of ether), when a vigorous reaction occurred, the yellow solid being replaced by a grey, granular precipitate. Ether (30 c.c.) was then added, the mixture heated on the water-bath for five hours, the ether removed, ice added, and the mixture distilled with steam. The volatile product (6·5 grams) was twice fractionated, yielding 2·7 grams of bromobenzene,* which boiled at 150—160° on redistillation and was converted into *p*-bromonitrobenzene. Only traces of diphenyl were isolated. The residue (16·5 grams) after steam distillation was extracted with benzene, leaving 1 gram of inorganic matter and yielding 12 grams of almost pure tri-α-naphthylbismuthine. The benzene mother-liquor finally gave a friable solid, which melted at about 95° and on extraction with alcohol appeared to contain traces of diphenyl-α-naphthylbismuthine.

(II) The dibromide (3·75 grams) and 1 mol. of the Grignard reagent showed no apparent reaction in the cold. After six hours on the water-bath the product was extracted twice with benzene. The first extract yielded yellow crystals containing halogen, m. p. 210°, after recrystallisation from chloroform–ether (α-naphthyldibromobismuthine). Unchanged dibromide was obtained from the second extraction. Similarly from the interaction of triphenyl-

* The absence of free bromobenzene in the standard Grignard solution employed was established by a blank experiment.

bismuthine dichloride and magnesium phenyl bromide (1 mol.) some dichloride was recovered unchanged.

Action of Magnesium Methyl Iodide on Tri-α-naphthylbismuthine Dibromide.

With 3·2 grams of the dibromide and 1·5 mols. of the Grignard reagent the ether boiled rapidly and a deep red product was formed. After an hour on the water-bath and removal of the ether, it was extracted with dry chloroform. The yellow solution on addition of light petroleum gave tri-α-naphthylbismuthine.

Preparation of Triphenylbismuthine from Bismuth Bromide and Mercury Diphenyl.

On mixing mercury diphenyl (3·5 grams; 3 mols.), bismuth bromide (1·5 grams), and dry ether (25 c.c.), reaction was immediate and a flocculent, white precipitate was produced. After twelve hours the mixture was heated on the water-bath and filtered. The residue, mercury phenyl bromide, m. p. 273° (3·3 grams), was free from mercuric bromide. The ethereal solution yielded 1·6 grams of an oil, which quickly crystallised and was almost pure triphenylbismuthine. The yield was quantitative.

Interaction of α-Naphthyldibromobismuthine and Mercury Diphenyl.

The dibromobismuthine (18·5 grams, free from bismuth bromide) and mercury diphenyl (27·4 grams; 2 mols.) reacted very quickly when suspended in cold dry ether (60 c.c.), the yellow colour disappearing. On the next day dry benzene was added, the precipitate (28 grams) separated, and extracted twice with benzene. The residue (23 grams) was mercury phenyl bromide. The united extracts and filtrate gave an oil from which benzene and light petroleum separated a solid (*A*), m. p. 125—128°. The evaporated filtrate slowly solidified (10 grams). On solution in chloroform-alcohol a crystalline deposit (*B*), m. p. 67°, was obtained, from which similar treatment removed a white solid, m. p. 240°, which was free from bismuth and halogen, and gave naphthalene and mercuric chloride with hot hydrochloric acid. After recrystallisation from chloroform, it did not depress the m. p. of mercury di-α-naphthyl (241°). Further quantities were obtained from the intermediate fractions, which also contained some naphthalene and probably a certain amount of unchanged mercury diphenyl.

On concentration of the mother-liquor from *B*, and repeated

ractionation of the residue from dilute alcohol, a few grams of pure triphenylbismuthine were obtained and also about 0·2 gram of a crystalline bismuth compound, m. p. 95—100°, which was possibly crude diphenyl-α-naphthylbismuthine. A repetition of this reaction gave similar results.

Interaction of Tri-α-naphthylbismuthine Dibromide and Mercury Diphenyl.

The dibromide (22·1 grams), mercury diphenyl (20·8 grams; 2 mols.), and dry ether (50 c.c.) were well shaken, but after a week the mixture was still unchanged. This is in marked contrast with the behaviour of α-naphthyldibromobismuthine. The ether was then evaporated, dry benzene added, and the mixture boiled for two and a half hours. The yellow solid disappeared and 7·7 grams of mercury phenyl bromide (m. p. 275°) were deposited. The filtrate yielded 9·4 grams of a solid, m. p. about 200° (not sharp). After two extractions with acetone, to remove mercury diphenyl, and recrystallisation from benzene, this had m. p. 233—234° and did not depress the m. p. of tri-α-naphthylbismuthine.

The main benzene filtrate was evaporated, diluted with light petroleum, the deposit (m. p. 115—180°) extracted with acetone and recrystallised from benzene, yielding mercury di-α-naphthyl, m. p. 243°. The intermediate fractions contained mercury phenyl bromide. Concentration of the mother-liquors and treatment with light petroleum gave a solid (*A*) and an oil (*B*), from which by steam distillation about a gram of bromobenzene was isolated and converted into *p*-bromonitrobenzene. The non-volatile residue smelled very faintly of α-bromonaphthalene and on repeated fractionation from alcohol yielded 0·4 gram of pure triphenylbismuthine. The deposit *A*, after laborious treatment with various solvents, gave about 0·5 gram of impure diphenyl-α-naphthylbismuthine.

Action of Magnesium Methyl Iodide and Magnesium Phenyl Bromide on Triphenylarsine Dichloride.

(I) With the dichloride (3 grams) and magnesium methyl iodide (2 mols.) a red oil was deposited. After some hours the ether was evaporated, water added (which destroyed the red colour), and the mixture filtered. The residue (1·2 grams) on crystallisation from alcohol melted at 60° and was triphenylarsine. The aqueous liquid deposited colourless plates free from halogen, m. p. about 11[illegible] on rapid heating, but 200°, sintering from 113°, on slow heating

these are the properties of triphenylarsine dihydroxide (Phillips, *Ber.*, 1886, **19**, 1032).

(II) With magnesium phenyl bromide (2·5 mols.) and the dichloride (13 grams) suspended in dry ether, a vigorous reaction occurred and a granular precipitate was formed. After four hours on the water-bath the mixture was distilled with steam, the residue filtered, and extracted with alcohol, whereby 6·6 grams of *triphenylarsine*, m. p. 57—59°, were obtained.

The use of 1·5 mols. of the Grignard reagent also gave triphenylarsine.

Action of Magnesium Methyl Iodide and Magnesium Phenyl Bromide on Triphenylstibine Dichloride.

Twelve grams of the dichloride were covered with dry ether and magnesium methyl iodide (2·5 mols.) was slowly added. A violent effervescence occurred and a light brown, pasty mass separated, which with more Grignard reagent became white and almost disappeared. After four hours on a water-bath, distillation with steam yielded iodobenzene, from which at least two grams of the iodo-dichloride were isolated. Extraction of the non-volatile residue with alcohol yielded 4·4 grams of triphenylstibine (m. p. 51—52°), which was characterised by conversion into the dibromide. The alcoholic mother-liquor gave about 0·1 gram of a pink, viscous residue, which crystallised from water or aqueous alcohol in colourless needles, m. p. 205—210°, decomposing at about 225°, giving a red sublimate. The production of this substance, possibly a stibonium derivative, is of interest, and the reaction is being investigated further.

With 1·5 mols. of the Grignard reagent in the cold no stibine could be isolated on addition of water, the product consisting of hydroxyhaloids of triphenylstibine, yielding the dichloride with concentrated hydrochloric acid.

Estimation of Halogen in Derivatives of the Types $BiRX_2$ *and* BiR_2X.

0·2 to 0·3 Gram of the substance is decomposed by warming with alcoholic ammonia for half an hour. The halogen is then precipitated by silver nitrate solution acidified with nitric acid. The method was tested on diphenylchlorobismuthine (Found: Cl=8·97, 8·88. Calc., Cl=8·97 per cent.).

The authors desire to express their thanks to the Research Fund of the Chemical Society for a grant in aid of this investigation.

and to Messrs. Thomas Tyrer & Co., Ltd., of Stratford, E., for specially preparing the anhydrous bismuth chloride which was required.

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[Received, April 21st, 1921.]

CIII.—*Some Factors Governing the Sorptive Capacity of Charcoal. Sorption of Ammonia by Cocoa-nut Charcoal.*

By JAMES BRIERLEY FIRTH.

IN a previous paper (Firth, *Zeitsch. physikal. Chem.*, 1914, **86**, 307), the author pointed out the great difference in activity of the cocoa-nut charcoals used by various experimenters, even although th(methods of preparation and treatment were very similar. Thus in the case of the sorption of hydrogen at liquid-air temperatures Travers (*Proc. Roy. Soc.*, 1906, **78**, 9) obtained the values 7·3 c.c at 12 mm. and 16·7 c.c. at 248 mm.; McBain (*Phil. Mag.*, 190[9] [vi], **18**, 916), 23·5 c.c. at 10 mm.; Firth (*loc. cit.*), 30 c.c. a 12 mm. and 78 c.c. at 241 mm. per gram of charcoal in each case.

This wide difference in activity of the charcoals required furth(investigation, and it was with the object of determining some (the factors which govern the activity that the present investigati(was undertaken.

The earlier belief was that the most active charcoal was obtain(by carbonising at as low a temperature as possible with t[h] minimum amount of heating. Hunter (*Phil. Mag.*, 1863, [iv], **2** 365) observed that different samples of similarly prepared charco(had different activities, which he explains thus: "The variatio in the amount of absorption are probably due in part to the slig differences which must exist in the pores of different pieces of t same charcoal and also to unavoidable differences in the heati of the charcoals in each experiment.

"In order to determine the effect of long-continued heat on absorbing power of the charcoal I kept a piece of boxwood charc at a strong red heat for upwards of an hour, after which its absorpt for ammonia was found to be 79, while in the ordinary way it was 8

Travers (*loc. cit.*) states that "if the charcoal has been too strongly heated, it loses its power of absorbing colouring matters and, indeed, substances generally either in the gaseous state or in solution, and this may be explained by the fact that the action of heat results either in the partial conversion of the carbon into a more stable crystalline phase, into which substances diffuse less readily, or in causing it to become more compact, in which case the surface is limited and each 'diffusion column' becomes longer." If this statement is correct, it will be highly probable that such a partial conversion will involve a change in the density of the charcoal, and one may reasonably look for a continuous change in activity with change in density. Hence the first experiments had for their object the determination of the relation (if any) between the temperature at which the charcoal had been heated, the duration of heating, the change in density, and the activity.

Winter and Baker (T., 1920, **117**, 320) have shown that, in the case of sugar-carbon which has been heated for forty hours at 900°, the density increases from 1·76—1·84, and by the same treatment the amount of sulphur dioxide "absorbed" increases from 97 c.c. to 288 c.c.

The charcoal used in the present investigation was obtained from cocoa-nut shell. The gas chosen was ammonia, since it can readily be obtained pure, and the amount sorbed is considerable. Saussure (*Ann. Physik* [Gilbert], 1814, **47**, 112) found that beech-wood charcoal sorbed ninety times its volume of ammonia at 12° and 724 mm. Hunter (*Phil. Mag.*, 1865, [iv], **29**, 116) found that cocoa-nut-shell charcoal sorbed 171·7 volumes of ammonia at 0° and 760 mm.

EXPERIMENTAL.

The essential part of the apparatus was the same as that already described in the case of the sorption of hydrogen (Firth, *loc. cit.*).

The carbon was prepared by carbonising cocoa-nut shell at as low a temperature as possible. The carbon obtained was exceedingly hard and dense and difficult to powder, and gave 0·91 per cent. of ash. It was then digested several times with hot, concentrated hydrochloric acid, boiled with distilled water, and washed free from chloride. The percentage of ash was now 0·39, and further treatment of the charcoal did not appreciably reduce this value. The carbon was then finely powdered and sieved. The ammonia was prepared from concentrated ammonia solution. The gas was passed through a hard glass tube, containing lime at a red heat, into pure hydrochloric acid, whereby pure ammonium chloride was obtained. This was heated with a solution of sodium

hydroxide and the resulting ammonia passed through large towers, containing calcium oxide and solid potassium hydroxide, into a large bulb, which served as a reservoir. Measurements were made at three temperatures, 18°, 0°, and −20°. The temperature −20° was obtained by stirring solid carbon dioxide into a bath of alcohol contained in a vacuum vessel, this being further protected by surrounding it with a box packed with cotton-wool. Solid carbon dioxide was added in small quantities from time to time.

The charcoal was heated at different temperatures for various periods. After each heating, the density was determined and then the sorptive capacity at each of the three temperatures, 18°, 0°, and −20°. The temperature at which the charcoal was heated was approximately determined by means of a pyrometer.

No matter what the previous treatment of the charcoal may have been, when transferred to the sorption apparatus it was invariably heated at a dull red heat in a vacuum for two hours, allowed to cool to the temperature of the bath, and then ammonia admitted.

At 0° and at −20°, the sorption was very rapid during the first few minutes, whereas at 18°, after the initial exposure, the sorption was more gradual. In all cases the sorption became extremely slow after the first hour, being complete in about thirty-six hours.

The volumes given refer to one gram of the charcoal in each case and are corrected to N.T.P.

First Series.

Charcoal heated at 600°.

Period of heating. Hours.	Density.	C.c. of gas sorbed per gram of charcoal. 18°.	0°.	−20°.
6	1·685	73·7	109·8	138·5
12	1·688	91·4	129·3	157·9
24	1·691	103·8	141·9	172·3
48	1·708	131·6	162·4	197·6

It is evident from these experiments that continued heating ha considerably increased the activity of the charcoal, whilst th density has been slightly increased.

Second Series.

Charcoal heated at about 875—900°.

Period of heating. Hours.	Density.	C.c. of gas sorbed per gram of charcoal. 18°.	0°.	−20°.
6	1·712	143·8	188·4	221·7
12	1·752	173·8	223·6	269·8
24	1·801	203·1	256·3	298·4
[illegible]	[illegible]	211·7	268·3	317·8

Heating at 900° has produced a further increase in sorptive capacity, and at the same time the density has been appreciably increased.

A portion of the charcoal which had been heated at 900° for forty-eight hours and had D 1·825 was set aside for three months in a stoppered bottle, after which period its sorptive capacity was redetermined (it was heated at 600° in a vacuum for two hours before exposure to ammonia, as in previous experiments), with the following results:

18°, 185·5 c.c.; 0°, 254·2 c.c.; −20°, 303·1 c.c.

A quantity of charcoal was heated at 875—900° for seven days, with the result that the density increased to 1·985, and the sorption values were:

18°, 193·2 c.c.; 0°, 249·6 c.c.; −20°, 302·1 c.c.

Third Series.

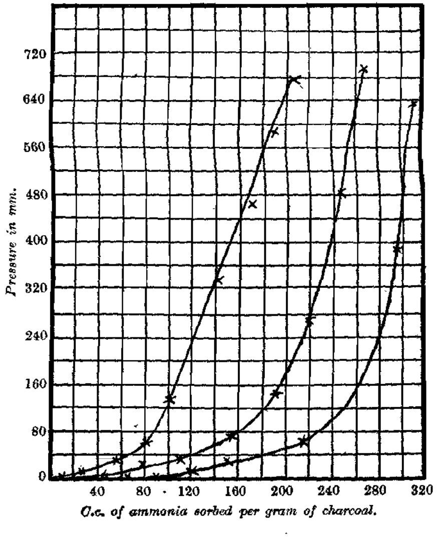
Charcoal heated at about 1050°.

Period of heating. *Hours.*	*Density.*	C.c. of gas sorbed per gram of charcoal. 18°.	0°.	−20°.
3	1·782	178·3	230·2	281·4
12	1·914	175·1	230·5	288·3
24	2·116	153·5	207·9	254·8

The experiments show that charcoal can be considerably activated by prolonged heating. At 600°, a considerable increase in the amount of gas sorbed is obtained without a very great change in the density. At 900°, a much greater increase is obtained, which is coincident with an appreciable increase of density. Further experiments show that increase of density does not necessarily mean increased activity. It would appear from the results that prolonged heating at 900°, or heating at higher temperatures, tends to convert the carbon into a denser form with diminished sorptive capacity, and that the observed density is merely an average value dependent on the proportion of each form. Hence increase of density may result in diminished activity. Further, when the charcoal is rapidly brought to a high temperature (above 1000°), a portion of the carbon may be converted into the denser form, whilst the bulk of the carbon has not materially changed. In this case the density may coincide with that of a carbon which has been heated, not so strongly, but for a longer period; yet the two forms would have very different sorptive capacities (compare series II and III). Hence density cannot be regarded as the criterion of activity.

It would appear also from the results that the activity of the carbon deteriorates with time. The results in general show that it is necessary to know the history of a charcoal, and a record of the density of the carbons used would make the results obtained by various experimenters more comparable, particularly in cases where the carbon has not been too strongly heated and consequently the formation or presence of the denser carbon is not very probable.

FIG. 1.



Determination of Equilibrium Pressures.

The equilibrium pressures at 18°, 0°, and −20° were determin The carbon used in these experiments had D 1·825, and obtained by heating the charcoal at about 900° for forty-ei hours, being a portion of the sample used in series II ab ... volumes of ammonia were admitted into the appar

until equilibrium was established. The results are set out in the following table and are shown graphically in Fig. 1.

18°.		0°.		−20°.	
C.c. of NH_3 per gram of charcoal.	Pressure in mm.	C.c. of NH_3 per gram of charcoal.	Pressure in mm.	C.c. of NH_3 per gram of charcoal.	Pressure in mm.
10·5	3·8	21·2	2·8	35·8	3·1
26·2	11·5	43·6	8·7	65·3	3·5
56·1	29·8	79·2	24·8	91·2	5·8
81·1	59·2	111·5	32·6	120·6	14·5
102·5	131·3	153·1	75·0	150·3	29·2
142·3	332·5	190·0	134·8	214·0	60·2
170·2	464·2	220·2	271·0	251·3	119·8
191·2	586·1	244·6	482·3	293·0	388·8
205·2	674·8	265·1	692·3	309·0	635·0

In the case of the isothermals at 0° and −20°, the lower portion of the curve indicates that a considerable increase in the volume of the gas sorbed makes only a small change in the equilibrium pressure, but after a certain point the conditions are reversed and a small change in the volume of the ammonia in the charcoal considerably increases the equilibrium pressure. This becomes more pronounced with lowering of temperature. The curves are very similar in character to those given by Travers (*Proc. Roy. Soc.*, 1906, **78**, 15) for carbon dioxide.

Summary.

Cocoa-nut charcoal carbonised at as low a temperature as possible and then heated at 600—900° increases considerably in activity within certain limits.

The density is also increased by the same treatment.

When the charcoal has been strongly heated, the density increases, but the activity diminishes. This is due to the formation of a more compact form of carbon of higher density but of diminished sorptive capacity.

The equilibrium pressures at 18°, 0°, and −20° have been recorded.

THE CHEMICAL DEPARTMENT,
UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, April 7th, 1921.*]

XIV.—*A Colloid Theory of the Corrosion and Passivity of Iron, and of the Oxidation of Ferrous Salts.*

By John Albert Newton Friend.

Among the numerous theories that have been advanced to account for the corrosion of iron, two, only, merit serious consideration. According to Whitney (*J. Amer. Chem. Soc.*, 1903, **25**, 394), pure iron will corrode in contact with pure liquid water and oxygen, because the water is slightly ionised. It is assumed that the iron passes into solution as iron ions, an equivalent quantity of free hydrogen being liberated. Thus :

$$Fe + 2H^{\cdot} + 2OH' \rightleftharpoons Fe^{\cdot\cdot} + 2OH' + H_2.$$

Ferrous hydroxide thus virtually exists in solution, and undergoes rapid oxidation in contact with gaseous oxygen to form rust.

According to the second and older theory, pure iron will not corrode under the above conditions, perfectly pure water not being regarded as an electrolyte. The presence of a fourth substance, an electrolyte, is regarded as essential. This theory has received strong support from the researches of Moody (T., 1906, **89**, 720) and the present author (see Friend, "The Corrosion of Iron and Steel," 1911, where a summary of the various researches is given) It also harmonises with the remarkable fact that as the methods of preparing pure substances become increasingly refined, the number of reactions known to occur between impure reagents but not between them when in a state of high purity, is steadily increasing.

Owing to the fact, known to Berzelius, that alkalis tend to inhibit corrosion, it was originally assumed that the electrolyte necessary to stimulate corrosion must be a free acid. In most cases of atmospheric corrosion carbonic acid was regarded as the active agent as was first clearly stated by Calvert (*Chem. News*, 1871, **23**, 9[illegible] Friend, *ibid.*, 1911, **103**, 138). The fact, however, that weak alkaline solutions of many salts readily induce corrosion dispose of the idea that the acid must necessarily be present in the free state.

Whatever the electrolyte may be, the final result is the same, that the iron passes into solution as a ferrous compound, underg[oes] oxidation, and is finally precipitated as rust.

Unfortunately, Whitney's theory is frequently termed "electrolytic" theory of corrosion; this is misleading and

led to much confusion, because by implication the second theory is not to be regarded as electrolytic. As we have seen, however, both theories are capable of electrolytic interpretation. The difference between the two theories, however, is more apparent than real, inasmuch as the absolutely pure substances are practically unobtainable, so that iron invariably rusts in contact with distilled water and air.

For some eleven years the author has realised that neither of the foregoing theories is in itself sufficient to account for all the phenomena attendant upon the corrosion of iron. The object of the present communication is to direct attention to a few important observations which cannot be explained by any known theory, and to suggest a new theory which appears to account for the facts in a reasonable manner.

The Corrosion of Iron in Moving Water.

In 1910, Heyn and Bauer (*Mitt. königl. Materialprüfungsamt*, 1910, **28**, 62) directed attention to the fact that, whilst a gentle movement of the water in which iron is immersed tends to accelerate greatly the rate of corrosion, a maximum effect is soon reached, after which a further increase in the velocity of the water causes a marked falling off in the rate of corrosion. The method of experiment consisted in causing water to flow rapidly through a glass tube into a beaker of 600 c.c. capacity in which two mild steel plates were suspended from a glass rod. The plates were separately weighed before and after the experiments, which lasted twenty-one days, the loss in weight caused by removal of the rust prior to the final weighing being taken as a measure of the corrosion. This method did not permit of the attainment of very high velocities, the maximnm being 350 litres per hour, corresponding approximately with a rate of flow across the surface of the metals of 1/20 mile per hour.

It seemed of interest to determine whether or not by greatly increasing the velocity of the water corrosion could be inhibited entirely. A strip of Kahlbaum's pure electrolytic foil was fixed, by means of a thin platinum wire, in a glass tube about 30 cm. long and 0·8 cm. internal diameter, joined by wired pressure tubing to a water-main tap. The foil measured $3 \times 0{\cdot}5$ sq. cm. in area and weighed approximately 0·35 gram. It was possible to cause the water to pass over the surface of the metal at any velocity up to 6 miles per hour, and to keep the surface of the metal under observation during the whole time. The results were as follow:

TABLE I.

Duration of the experiment. Hours.	Velocity of the water in feet/hour.	Loss in weight of the iron per hour. Mg.	Remarks.
22	0	0·082	Rust
24	540	0·188	"
22	570	0·177	"
24	4,200	0·054	Thin streams of rust
24	9,000	0·029	Traces of rust
25	13,000	0·032	" " "
22	30,000	0·045	No corrosion

It is thus evident that, if the velocity of the water is increased sufficiently, no corrosion of the metal, in the ordinary acceptation of the term, will take place. At very high velocities, the loss in weight shows a slight increase, due probably to mechanical erosion. The experiment was varied by introducing a small filter-pump between the water-main tap and the glass tube, so that varying amounts of air could be drawn into the tube. The surface of the metal was thus swept with water, milky with minute bubbles of air. The results were as follow:

TABLE II.

Duration of the experiment. Hours.	Velocity of the air + water in feet/hour.	Loss in weight of the iron per hour. Mg.	Remarks.
18	5,760	0·034	Rust
4	6,600	0·075	"
23	7,260	0·044	Slight rust
23	13,500	0·022	" "
24·5	11,160	0·033	Trace of rust in contact with the glass

In this series of experiments the difficulty lay in preventing bubbles of air from clinging to the metal at points of contact with the platinum wire or glass support, causing local corrosion. Apart from the effects of this, the results of the two series are substantially the same, showing that the freedom from rust is not due to shortage of oxygen.

Now, when rapidly moving iron is exposed to the action of dilute sulphuric acid, the rate of solution of the metal appears to be proportional to the velocity, even when the latter reaches the high value of from 30 to 40 miles an hour (unpublished experiments by Mr. T. H. Dennett, B.Sc., and the author). It appears, therefore ... solution is a different problem

from the dissolution of the metal in an acid. That such is the case will be made evident later.

These results, which were obtained with Worcester City tap water, appeared so remarkable that the author requested his friend, Dr. W. H. Hatfield of the Brown Firth Research Laboratory, Sheffield, to repeat the experiments with Sheffield water. This was the more desirable as Worcester water, which is drawn from the Severn, usually contains an abnormal amount of dissolved salts, notably sodium chloride, consequent upon the proximity of the Droitwich Salt Works and Brine Baths. Although the presence of this salt might be expected to enhance the corrosive action of the water, it was still possible that some other impurity was causing it to behave in an unusual manner. Repetition of the experiments with distilled water was clearly impossible in view of the enormous quantities required. The following is Dr. Hatfield's report.

"The samples of foil were polished to 000 emery paper and suspended by platinum wire in a glass tube of suitable diameter, as suggested. The period of test was forty-eight hours in each case. The temperature of the water was constant at 8° during the whole test. In the test with water at high velocity the rate of flow varied with a minimum of 2·02 miles per hour (during the day) to a maximum of 5·17 miles per hour (during the night). In the test with water at low velocity the rate of flow varied from 1/10 to 1/8 mile per hour."

The results were as follow:

(I) With water at high velocity, *no rust formed.* Loss in weight= 0·0013 gram or 0·014 gram per sq. dcm.

(II) With water at low velocity, definite corrosion took place. Loss in weight=0·0080 gram or 0·109 gram per sq. dcm.

These results confirm those of the present author.

The foregoing method, however, possesses many disadvantages in manipulation. The amount of iron taken is necessarily small, so that any alterations in weight are only measurable with a relatively high percentage error. Further, neither the temperature nor the composition of the water can be controlled.

It was thought that further light might be thrown on these remarkable results by determining the potential difference between iron and platinum wires immersed in dilute solutions of electrolytes both at rest and in motion. In order to avoid any possible purely thermal effects, the iron and platinum wires were kept stationary and attached either to a galvanometer or a millivoltmeter, and the vessel containing the solution was rotated. Slight movement caused a rise in the potential difference, but a maximum was soon attained, after which further increase in velocity caused the *P.D.*

to fall to a practically constant value almost uninfluenced by the application of still higher velocities. When expressed as a *P.D.*–velocity curve, the results were found closely to resemble the corrosion–velocity curve drawn from the data in Table I.

For reasons which will appear later, the constant *P.D.* at high velocity probably represents the *true* solution *P.D.* between iron and platinum in the electrolyte.

Since the rapidly moving water inhibits corrosion, it would appear that it sweeps away from the surface of the metal some catalyst which assists the metal to corrode, and in the absence of which the metal simply dissolves in the liquid ionically with such small velocity that it is almost "passive." This catalyst must be derived from the iron, and the author believes it to be the hydrosol of iron hydroxide.

It is therefore suggested that:

1. Iron is "noble" or passive towards distilled water in the absence of a catalyst and passes into solution, but only with extreme slowness, owing to the traces of electrolytes that are present.

2. The dissolved iron is probably at first present in a more o less completely ionised ferrous condition, but is rapidly converte into the sol of ferrous hydroxide.

3. This sol then undergoes oxidation by dissolved oxygen int the sol of a higher hydroxide, ferric hydroxide sol being forme under the most favourable conditions, and probably ferroso-ferr hydroxide sol when the supply of oxygen is limited.

4. The higher hydroxide sol now acts catalytically by oxidisi metallic iron with relative rapidity and simultaneously undergoi reduction to a lower hydroxide sol, only to be oxidised again oxygen from the air diffuses towards it. This is quite in harmo with the known catalytic activity of ferric hydroxide and with t observation that "nascent" ferrous hydroxide is a more power reducing agent than the precipitated compound (Baudisch, *B* 1921, **54**, [B], 406).

If this theory is correct, it will be evident that the rate of corros of iron must be dependent upon sol formation. If, therefore, sol is removed from contact with the iron as rapidly as it is form as, for example, with flowing water, corrosion must be inhibit The same retardation will clearly be effected if the colloid is coa lated either by physical, including electrical, processes or chemical precipitants.

A ready means of testing the theory therefore lies in determi whether or not the phenomena of corrosion are influenced by factors as affect the formation, stability and precipitation, ... electropositive colloid

particular, since metallic hydroxide sols are usually positive in character.

Influence of Dissolved Electrolytes upon Corrosion.

The addition of small quantities of many salts greatly enhances the corrosive action of water upon iron, a maximum effect being reached at what is termed the "critical concentration" (Heyn and Bauer, *loc. cit.*, 1908, **26**, 1). Further addition of the electrolyte tends to reduce the corrosion, which may fall to nil at the "limiting concentration." In most cases, however, saturation is reached before the limiting concentration, which therefore becomes a hypothetical value; it may be determined approximately by extrapolation from the concentration–corrosion curve, and is sometimes of use.

Adie (*Min. Proc. Inst. Civil Eng.*, 1845, **4**, 323) explained the fall in corrosion in the case of brine on the ground of the reduced solubility of oxygen in the solution. This theory received support from the later work of Walker and his co-workers (*J. Amer. Chem. Soc.*, 1907, **29**, 1251), who showed that the rate of corrosion of iron is proportional to the concentration of the dissolved oxygen.

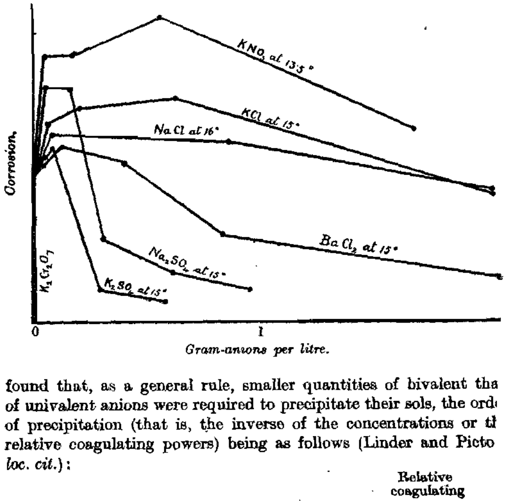
During 1911—1915 the results were published of several series of investigations into the corrosive action of many common salt solutions upon iron at various temperatures. From a study of these (Friend and Brown, T., 1911, **99**, 1302; *J. Iron Steel Inst.*, 1911, I, 125; Friend and Barnet, *ibid.*, 1915, I, 336; Friend, *ibid.*, Carnegie *Schol. Mem.*, 1911, III) it is at once evident that, although the reduced oxygen solubility is an important factor, it cannot be the only one, inasmuch as the diminution in corrosion is usually very much greater than the theory requires. Thus, for example, the relative corrosions of iron (as measured by loss in weight) in distilled water and in saturated potassium sulphate solution at 15° were, in a particular experiment, 100 and 14 respectively, whilst the relative solubilities of oxygen in these liquids are 100 and 67·3.

It so happens that all the concentrations employed in these researches were expressed as grams per litre, with the result that several remarkable features were overlooked. If, however, the concentrations are converted into gram-anions per litre and corrosion–concentration curves drawn for different salts at comparable temperatures, as in Fig. 1, the corrosion of iron in distilled water being taken as 100 and all other corrosions being expressed relatively thereto, several points of very great interest become apparent. It is seen that the action of the electrolytes is mainly influenced by the character of the anions. Whilst very small concentrations of

dichromates entirely inhibit the corrosion of iron, large quantities of the chlorides and nitrates are required to produce an appreciable diminution of corrosion. The sulphates lie intermediately, small quantities effecting a marked diminution in corrosion, although not entirely inhibiting it.

These results bear a striking resemblance to those obtained by Hardy (*Proc. Roy. Soc.*, 1900, **66**, 95, 110; *Zeitsch. physikal. Chem.*, 1900, **37**, 385), Freundlich (*ibid.*, 1903, **44**, 144), and Linder and Picton (T., 1905, **87**, 1906) on the precipitating effect of these salts upon ferric hydroxide hydrosol. Thus all these investigators

FIG. 1.



found that, as a general rule, smaller quantities of bivalent tha[n] of univalent anions were required to precipitate their sols, the ord[er] of precipitation (that is, the inverse of the concentrations or th[e] relative coagulating powers) being as follows (Linder and Picto[n], *loc. cit.*):

	Relative coagulating power.
Chlorides and nitrates (about equal)	0·3
Sulphates	67
Chromates and dichromates	100

This is in excellent agreement with the general slopes of t[he] curves in the figure.

... undoubtedly exerts an influence. Thus Ha

observed that the concentration of barium chloride required to precipitate his sol lay intermediately between that of sodium chloride and potassium sulphate—a result showing an interesting parallel to that in the figure.

These observations are regarded by the author as strongly supporting his colloid theory of corrosion. The initial rise in corrosion on addition of a small quantity of a salt is due to the increased solvent action of the liquid. As the concentration increases, the effect of the enhanced solubility is counteracted, not only by the reduced solubility of oxygen, but also by the precipitation of the catalysing sol, with the result that the corrosion reaches a maximum and then begins to fall.

Influence of Protective Colloids.

It is well known that protective colloids exert a marked retarding influence upon the catalytic activities of suspensoid colloids. This has been studied more particularly in connexion with the decomposition of hydrogen peroxide by colloidal platinum. Assuming the colloid theory of corrosion to be correct, a general similarity should exist between this phenomenon and the rate of corrosion in the presence of protective colloids. This has been found to be the case.

I. Different protective colloids exert very varying inhibiting influences upon the rate of corrosion of iron, as is evident from a consideration of the results in columns 2, 3, and 4 of Table III. These results were obtained by determining the losses in weight sustained by small plates of Kahlbaum's foil after immersion for

TABLE III.

Colloid 0·2 per cent.	Loss in weight of the iron. Mg.	Mean losses. Mg.	Relative corrosion.	Protection factor.	Relative rates of H_2O_2 decomp. (Iredale).	Zsigmondy gold numbers.
Water	35·1 35·4	35·3	100	1	100	∞
Sucrose	31·7 32·2	32·0	91	1·1	100	∞
Gum acacia ...	19·2 24·6	21·9	63	1·6	52	0·5—4·0
Starch (Potato)	17·0 17·4	17·2	50	2·0	50	25
Dextrin	17·6 17·4	17·5	50	2·0	37	10—20
Gelatin	17·0 18·0	17·5	50	2·0	17	0·005—0·001
Egg-albumin ...	10·3 9·5	9·9	28	3·7	23	0·15—0·25
Agar	3·5	3·5	10	10·0	—	—

sixteen days in 0·2 per cent. solutions of the various colloids in water, at a mean temperature of 10°. The experiments were carried out in duplicate. In column 4 the mean loss in weight of the irons in water is taken as 100, the losses in the other solutions being expressed relatively thereto.

In column 6 are given Iredale's results for the inhibiting action of 0·01 per cent. solutions of the same colloids upon the rate of decomposition of hydrogen peroxide by colloidal platinum (Iredale, this vol., p. 109. Also Groh, *Zeitsch. physikal. Chem.*, 1914, **88**, 414). It will be observed that a very close similarity exists between the two series of results. The only exception is gelatin, and reference to this will be made later.

In column 5 are given what may be termed the protection factors of the colloids, obtained as follows :

$$\text{Protection factor} = \frac{100}{\text{Relative corrosion}}.$$

Both Groh and Iredale have pointed out that the inhibiting action of protective colloids increases in general with the protective properties of the same, although there appears to be no precise mathematical relation between the two. A general similarity, however, can be traced between Zsigmondy's gold numbers (given in column 7 of Table III) and the inhibitive action.

It is not at all improbable that the inhibiting action is directly proportional to the protective power of a colloid, and any discrepancies in the above table may be explained as follows :

(1) The colloids are natural substances, and different samples vary considerably. Since the same specimens could not be used by the three above-named investigators, some differences are to be expected. This is particularly the case with gum acacia (arabic), which is one exhibiting exceptional behaviour, for this commercial product is frequently a mixture of several varieties, possessing different properties. Zsigmondy obtained values ranging from 0·1 to 4 for the gold numbers of different samples of this gum (*loc. cit.*).

(2) The concentrations of the colloids were different in the several series. As shown later, the concentration–inhibition curves for colloids are not always straight lines, so that the relative values may vary with the concentration.

(3) Zsigmondy's gold numbers represent the various concentrations of colloids possessing equal protective power, and this is not necessarily the same problem as the relative protective powers at a given concentration.

(4) The corrosion experiments must necessarily be extended over

at least ten days in order to give measurable results, and during this time not only do the colloids tend to settle, but the less stable ones are liable to undergo a certain amount of decomposition. The latter is particularly the case with egg-albumin, the author's solution being fœtid after the sixteen days' test described above. Zsigmondy directs attention to the same point, finding with dextrin and glue a distinct rise in the gold number after a few days.

2. The extent of retardation depends on the concentration of the protective colloid. Thus Groh (*loc. cit.*) found that by increasing the amount of gelatin from 0·001 to 0·10 per cent. the activity of colloidal platinum was reduced to less than one-half.

Analogous results have been obtained with agar and gum acacia on the corrosion of iron, as is evident from Table IV.

TABLE IV.*

Colloid.	Per cent.	Loss in weight of the iron. Mg.	Relative corrosion.
Agar	0·20	3·5	10
	0·10	6·4	18
	0·02	22·0	63
	0·00	35·3	100
Acacia	2·5	11·2	32
	1·0	14·0	40
	0·5	18·5	53
	0·2	21·0	63
	0·1	32·4	92
	0·0	35·3	100

When these results are shown graphically, along with those of Groh, it will be observed that the curves are not straight lines, so that the *relative effects of different colloids at various concentrations* will not necessarily be constant.

The foregoing results are very striking, for reactions involving a soluble catalyst do not appear to be affected by the presence of a protective colloid. Thus agar has no influence upon the velocity of the acid catalysis of methyl acetate (Reformatsky, *Zeitsch. physikal. Chem.*, 1891, **7**, 34). This lends support to the view that the catalyst assisting corrosion is not a soluble iron compound.

The Action of Alkalis.

The inhibiting action of alkalis upon corrosion is usually attributed to the presence of the hydroxyl ions causing a suppression of aqueous ionisation (Whitney, *loc. cit.*), so that the equilibrium,

$$Fe+2H^{\cdot}+2OH' \rightleftharpoons Fe^{\cdot\cdot}+2OH'+H_2,$$

* Experiments carried out with Kahlbaum's foil, immersed in the colloid solutions for sixteen days at 10°.

is moved in the direction from right to left. Alkali carbonates are presumed to react similarly, since they consist of a powerful base combined with a weak acid. Such an explanation, however, cannot be altogether correct, as it does not explain why dilute solutions of the alkali carbonates not merely fail to inhibit corrosion but actually cause the metal to corrode more rapidly than does distilled water (Heyn and Bauer, *loc. cit.*; Cribb and Arnaud, *Analyst*, 1905, **30**, 225). The colloid theory, however, disposes of this anomaly, for corrosion will be inhibited when the alkali is sufficiently concentrated to precipitate the catalytic sol as rapidly as it is formed. The precipitated oxide slowly dissolves in the alkali, presumably yielding a ferrite, and is precipitated ultimately as Fe_2O_3,xH_2O, but not on the surface of the metal, which remains bright throughout. In this manner is explained the slow solubility of iron in sodium hydroxide solutions, which the author has observed to take place in many concentrations of the hydroxide after the lapse of months or years, according to circumstances.

The Influence of Ethyl Alcohol.

The effect of addition of ethyl alcohol to water in which iron is corroding is interesting. Being a non-electrolyte, it should not be adsorbed to any appreciable extent. On the other hand, it possesses a considerable dehydrating power and is a typical example of that important class of precipitants which effect the coagulation of colloids through withdrawal of the solvent. It may thus be expected to reduce the stability of the sol and hence the rate of corrosion of the metal. Its effect upon the solubility of oxygen in the solution is relatively small. The following results were obtained with small plates of Kahlbaum's pure electrolytic foil immersed in the various solutions for twenty-nine days at 18°. The plates weighed approximately 1·7 grams, and measured 3×4 sq. cm.

TABLE V.

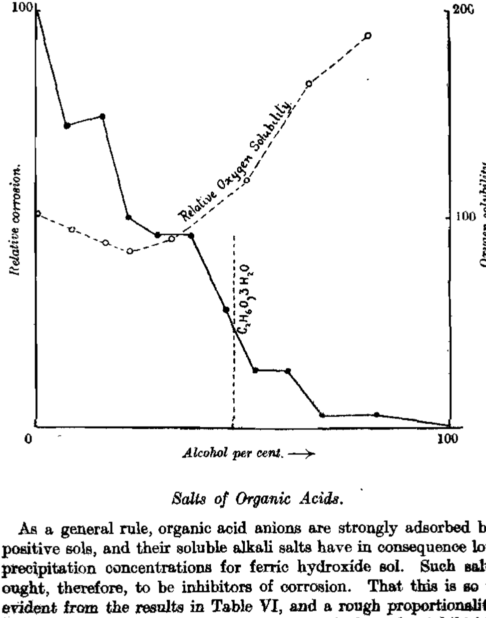
Alcohol. Per cent. by weight.	Loss in weight of the plate. Gram.	Relative corrosion.	Alcohol. Per cent. by weight.	Loss in weight of the plate. Gram.	Relative corrosion.
0	0·555	100	44·4	0·155	28
8	0·400	72	52·1	0·075	14
16·3	0·415	75	60·3	0·080	14
23·0	0·275	50	69·0	0·020	3
29·9	0·255	46	80·7	0·025	3
36·9	0·255	46	100·0	0·000	0

When these results are plotted on a corrosion–concentration diagram (Fig. 2), it becomes evident that but little corrosion occurs

after the concentration of the alcohol has passed that corresponding with the formation of the trihydrate, $C_2H_6O,3H_2O$. In pure alcohol there is no corrosion, there being no water to yield the catalytic hydrosol.

The relative solubility of oxygen in the solutions (reduced to half scale) is given by the broken line in the figure, and had this been the only factor or even merely the most important factor, the corrosion curve would have had an analogous form.

FIG. 2.



Salts of Organic Acids.

As a general rule, organic acid anions are strongly adsorbed by positive sols, and their soluble alkali salts have in consequence low precipitation concentrations for ferric hydroxide sol. Such salts ought, therefore, to be inhibitors of corrosion. That this is so is evident from the results in Table VI, and a rough proportionality is traceable between the concentrations of the salts inhibiting corrosion and the precipitation concentrations for ferric hydroxide sols as determined by Freundlich (*Kolloid Zeitsch.*, 1907, **1**, 321).

TABLE VI.

Sodium salt.	Approx. inhibiting concentration. Per cent.	Inhibiting concentration. Gram-mols. per litre.	Precipitation concentration. Milligram-mols. per litre.
Chloride	Sat. soln. corrodes	—	300
Formate	20	3·0	56
Acetate	4	0·30	30
Benzoate	2	0·14	32
Salicylate	2	0·13	20

The foregoing concentrations are only approximate and indicate that iron completely immersed in these solutions will not, in general, show ordinary corrosion within twenty-four hours. Frequently a few isolated spots of rust form, mainly at the edges of the metal, indicating some physical or chemical irregularity. After a few days the metal will probably show signs of general rusting, possibly through oxidation of the organic acid.

Poisons.

Both biological processes and the catalytic activities of colloidal metals may be diminished or even entirely destroyed by the addition of small quantities of certain substances termed "poisons." In both cases the inhibition appears to be connected with adsorption (see Wo. Ostwald and Dernoscheck, *Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 267, etc.).

Now, ferric hydroxide gel adsorbs arsenious oxide to a remarkable extent (see Biltz, *Ber.*, 1904, **37**, 3138; Lockemann, *Ver. Ges. Deut. Naturforsch. Aerzte*, 1911, **11**, 25; Boswell and Dickson, *J. Amer. Chem. Soc.*, 1918, **40**, 1793). It must be more than mere coincidence that arsenious oxide should be a powerful inhibitor of corrosion (Lindet, *Compt. rend.*, 1904, **139**, 859, whose results have been confirmed by numerous later investigators). If the colloid theory of corrosion is accepted, a fresh light is thrown upon this hitherto unexplained phenomenon. Sodium arsenite behaves similarly, and is frequently added to boiler-feed waters to reduce corrosion (Huntley, *J. Soc. Chem. Ind.*, 1909, **28**, 339).

Influence of Temperature.

Ferric hydroxide sol is very stable, and the liquid may be boiled under suitable conditions without precipitation. If, however, electrolytes are present, the colloid is readily precipitated. It is to be anticipated, therefore, that corrosion will not be accelerated so rapidly in the presence of electrolytes upon rise of temperature,

as in the case of water alone. Hence, relatively to water at the corresponding temperatures, the corrosive action of salt solutions may be expected to fall with rise of temperature. This serves to explain the remarkable observation (Friend and Brown, T., 1911, **99**, 1302) that, whilst at 11° sea-water is more corrosive than distilled water, at about room temperature the two are equally corrosive, whilst at 21° and above, sea-water is distinctly less corrosive than distilled water. Analogous results have been obtained with solutions of many other electrolytes (Friend and Barnet, *loc. cit.*). As a general rule it is found that the higher the inversion temperature, the lower is the corresponding salt concentration. It was further shown that the critical concentration likewise falls with rise of temperature. All these observations are in harmony with the present author's theory.

Radium Rays.

Many chemical reactions are accelerated by radium emanations, oxidation processes being particularly sensitive (see Creighton and Mackenzie, *Amer. Chem. J.*, 1908, **39**, 474; Pellini and Vaccari, *Atti R. Accad. Lincei*, 1904, [v], **13**, ii, 269; Reckleben and Lockemann, *Zeitsch. anorg. Chem.*, 1915, **92**, 145). If, therefore, the corrosion of iron is purely ionic or an example of direct oxidation, it is to be anticipated that the rate of corrosion will be increased by radium salts, particularly since their emanations decompose water, yielding hydrogen, oxygen, and hydrogen peroxide, β- and γ-rays being effective as well as α-rays (Kernbaum, *Compt. rend.*, 1909, **148**, 705; Debierne, *Ann. Physique*, 1914, [ix], **2**, 97; *Compt. rend.*, 1909, **148**, 703; Creighton, *Trans. Nova Scotia Inst. Sci.*, 1908, **12**, 34).

On the other hand, Jorissen and Woudstra (*Chem. Weekblad*, 1912, **9**, 340; confirmed by Fernau and Pauli, *Biochem. Zeitsch.*, 1915, **70**, 426) found that radium emanations tend to coagulate ferric hydroxide sol. If, therefore, the colloid theory of corrosion be accepted, the presence of radium salts should tend to retard corrosion. This has been demonstrated to be the case in a series of preliminary experiments.

Discs of Kahlbaum's iron foil (diam. 11·8 cm.) were immersed in water in shallow earthenware dishes, some serving as blanks whilst others were exposed to the influence of rays from about 0·1 mg. of radium chloride, contained in a metal capsule with a mica window, and suspended above the discs, window downwards.* The results were as follow :

* The author desires to express his thanks to Professor S. W. J. Smith of Birmingham University for kindly loaning him the radium salt.

TABLE VII.

Height of RaCl₂ above the disc. Cm.	Duration of the experiment. Hours.	Loss in weight of the disc under RaCl₂. Gram.	Loss in weight of the blank. Gram.	Relative corrosion of discs under RaCl₂ (Blank = 100
1·5	72	0·0388	0·0419	93
4·0	112	0·0667	0·0783	85
13·0	120	0·0444	0·0513	87

As the mica window held back the α-rays, the observed effect were due to β- and γ-rays. The apparently diminished action a 1·5 cm. is probably due to the rays being severely localised at th centre of the metal disc, not having room to spread out over th whole disc before striking the metal, as in the succeeding experiment

These results, obtained with such a feeble source of radioactiv rays, are highly interesting and further experiments are in progres

Analogous experiments were carried out with oxides of thoriur and uranium. Thirty grams of these were placed in thin-walle tubes and immersed in water surrounded by sheets of Kahlbaum' foil. The results were as follow:

	Loss in weight of the *iron in grams after* 5 days.	14 days.	Total loss *in weight.* (19 days.)	*Relative* losses.
Water only .... (mean of two blank experiments)	0·0722	0·1699	0·2421	100
With ThO_2	0·0686	0·1655	0·2341	97
With UO_2	0·0821	0·1722	0·2543	105

The activities of the radioactive specimens were very feeble a compared with that of the radium chloride, and the results corre spondingly indecisive. The thorium appears to retard corrosio and the uranium to accelerate it, very slightly.

Passivity.

In 1790 Keir (*Phil. Trans.*, 1790, **80**, 359) directed attention t the fact that iron immersed in nitric acid of density 1·45 is rendere passive or inert. It retains its metallic appearance and does no seem to dissolve, although actually it is passing into solution wit extreme slowness. It was soon observed that solutions in whic iron remained passive were powerful oxidisers (Schönbein an Faraday, *Phil. Mag.*, 1836, [iii], **9**, 53, 122; 1837, [iii], **10**, 175 and this led to the belief that a thin layer of oxide was forme on the surface of the metal, which protected the underlying portion from attack. But all passivifiers are not oxidisers, hydroxyl

acid being a case in point (Turrentine, *J. Amer. Chem. Soc.*, 1911, **33**, 803).

It does not appear to have been observed hitherto that all solutions which induce passivity contain anions of powerful precipitating activity towards positive colloids. The author therefore suggests that the passivifying action of various liquids on iron lies in the destruction of the catalysing sol.

In certain circumstances, for example, in nitric acid, the sol may be precipitated as a thin protective layer of oxide on the surface of the metal, thereby causing the latter to retain its passivity for a time when removed from the passivifying liquid and placed in water. But this is a secondary result and is not the cause of the inertness of the metal in the passivifying liquid itself.

The colloid theory of passivity offers explanations for many points of interest. It is known that nitric acid of density 1·250 does not render iron passive at 0°, yet if the temperature is raised to 10° or more the metal is readily passivified by it (Young and Hogg, *J. Physical Chem.*, 1915, **19**, 617). The explanation is analogous to that offered in the case of the diminished activity of sea-water and various electrolytic solutions as compared with distilled water with rise of temperature.

Oxidation of Ferrous Salts.

Solutions of ferrous salts, particularly in the presence of alkali, oxidise upon exposure to air with a velocity proportional to the pressure of the dissolved oxygen. The rate of oxidation is enhanced by light (Friend, West, and Bentley, *J. Iron Steel Inst.*, 1912, I, 259), but retarded by certain acids, such as sulphuric acid (Warynski, *Ann. Chim. Anal.*, 1909, **14**, 45).

The present author suggests that the oxidation of ferrous salts under these conditions is analogous to the corrosion of iron, being catalytically accelerated by an iron sol. Most probably the sol is, at any moment, a mixture of the different iron hydroxides, containing, no doubt, adsorbed anions from the acid radicle.

This theory receives support from a number of different observations, two of which may be cited.

(1) In 1899, Spring (*Bull. Acad. Roy. Belg.*, 1899, [iii], **37**, 174) directed attention to the fact that iron salts in neutral solution invariably give the Tyndall effect, showing that a hydrosol is present. The effect disappears on adding an acid, the sol apparently passing into solution.

(2) The addition of chemically neutral salts, such as sodium chloride or bromide, reduces the rate of oxidation (MacArthur,

J. Physical Chem., 1916, **20**, 545; Warynski, *loc. cit.*), but, as in the analogous case of the corrosion of iron, the retardation is greater than can be explained by mere diminution of the oxygen solubility. This is readily explained on the assumption that the sol undergoes precipitation by the dissolved salt, so that its catalytic power is diminished.

The converse of these reactions, namely, the reduction of ferric sulphate solution with zinc and magnesium, has been studied by Sugden (this vol., p. 233), and the curious results obtained appear capable of explanation by application of the author's colloid theory in an analogous way.

The Composition of the Sol.

The evidence at present available does not enable a definite decision to be arrived at as to the exact compositions of the catalysing sols. Most probably sols of ferrous, ferroso-ferric, and ferric hydroxide take part, being alternately oxidised and reduced from one to the other. Under favourable conditions ferric hydroxide sol is probably produced. But the following series of experiments appears to indicate that in a strictly limited supply of oxygen the higher sol may be only that of ferroso-ferric hydroxide.

Into a series of bottles of approximately 150 c.c. capacity were put weighed pieces of pure electrolytic iron foil and 100 c.c. of water, the remaining 50 c.c. being air. The stopper was coated with vaselin and later fixed in position with wax and the bottles kept in a dark cupboard. At intervals one or more were removed, the loss in weight of the iron was determined, and the amount of ferrous iron estimated by titration with permanganate. The results were as follow:

TABLE VIII.

Time (years).	Loss in weight of the iron. Gram.	Weight of ferrous iron. Gram.	Weight of ferrous iron. Per cent.
0·1	0·0356	trace	trace
0·5	0·0421	0·0050	11·8
3*	0·0518	0·0130	25·1
7·25*	0·0429	0·0129	30·0 (Fe_3O_4)

* Mean of several experiments.

General Application of Colloid Activity.

Most substances manifest a maximum chemical reactivity when in the colloidal state. It is not improbable, therefore, that many

eactions which have hitherto been ascribed to ions may be ex-
plained more readily on the autocolloid, catalytic theory. Many so-called catalysts, which are known to be chemically inert, may simply act by rendering possible the existence of a colloid catalyst formed from the reacting substances themselves. They are thus not true catalysts, in the sense of actually taking part in the reactions themselves, but may be termed *secondary* catalysts. For example, ammonia and hydrochloric acid when perfectly pure and dry do not interact with measurable velocity. The addition of benzene (Kahlenberg, *J. Physical Chem.*, 1902, 6, 1) causes instant combination. Application of the ionic theory in this case is strained. It is quite in accord with the behaviour of benzene, however, to suppose that it facilitates the formation and stabilisation of a colloidal form of ammonium chloride, which catalytically assists the union of the remaining HCl and NH_3 molecules. The benzene thus functions as a secondary catalyst.

A similar autocolloidal, catalytic explanation might be offered for numerous other reactions, and the author hopes to indicate its bearing upon the corrosion of ferrous alloys and non-ferrous metals.

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[*Received, March 16th*, 1921.]

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